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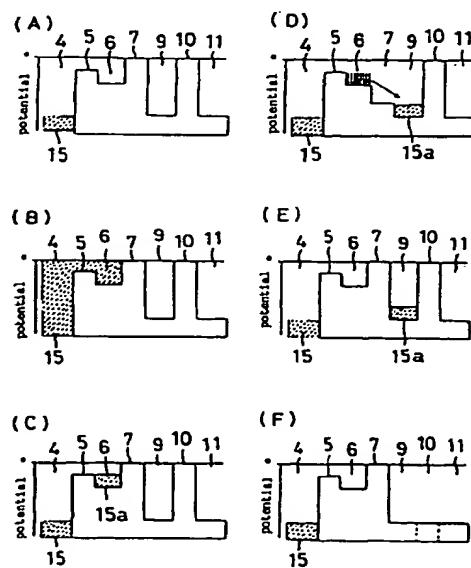
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(54) Method for measuring physical phenomena or chemical phenomena and equipment thereof

(57) To provide a method and an equipment that can easily visualize various physical phenomena or chemical phenomena by simultaneously taking in, accumulating, and transferring the information at a plurality of points.

Electric charges are injected in potential wells constructed to vary the depth in accord with the magnitude of the physical or chemical quantity, and the physical or chemical quantity is converted into electric charges according to the depth of the potential wells.

Fig. 3



Description

The present invention relates to a measuring method and equipment for quantifying various physical phenomena or chemical phenomena.

Conventionally, it is light that converts physical phenomena or chemical phenomena into electric charges for measurement. Irradiating photo-diodes with the light generates electron-hole pairs corresponding to the light quantity, and the light quantity is changed to quantity of electric charges, and the light quantity is measured by evaluating the quantity of electric charges.

However, in physical and chemical phenomena other than light, in almost all cases, they are converted to electric signals such as voltage values, electric current values, resistance values, etc., and these values are read.

For example, there are thermocouples using the Seebeck effect in which potential difference is generated on both ends when different temperatures are applied to both ends of a certain metal wire. This is intended to join two kinds of different metals and the temperature of the joined portion is determined from the potential difference generated at both ends. The measurement of pH using ISFET (Ion-sensitive field-effect transistor) is achieved by changing the channel conductance below the pH-sensitive gate insulator by absorbing the hydrogen ion, and measuring the pH value of the solution by measuring the drain current.

In either of the measurement methods illustrated above, accumulation and transfer, which are handling methods special to electric charges, are unable to be carried out, and it is extremely difficult to simultaneously take in information at a plurality of points and process at high speed or visualize the measurement results.

Now, for physical phenomena or chemical phenomena, there are various phenomena such as concentration, temperature, magnetic field, pressure, acceleration, velocity, sound wave, ultrasonic wave, oxidation-reduction potential, reaction velocity, etc., and these phenomena can be converted into various electric signal (current, voltage, resistance, capacity, potential) by the use of conventional technologies, but it is the main object of this invention to handle these phenomena in a manner special to electric charges by converting these phenomena into electric charges and to carry out quantification special to electric charges.

Therefore, it is an object of this invention to provide a method and equipment that can easily visualize various physical phenomena or chemical phenomena by simultaneously taking in data at a plurality of points and carrying out accumulation and transfer.

To solve this object the present invention provides a method and an equipment as specified in claims 1 and 3.

The method of measuring physical phenomena or chemical phenomena of this invention uses potential wells configured to change the depth corresponding to

the magnitude of the physical or chemical quantity, to inject electric charges into these potential wells, and to convert the physical or chemical amount to electric charges corresponding to the depth of the potential wells.

The equipment of measuring physical or chemical phenomena of this invention is configured to one-dimensionally or two-dimensionally array a plurality of potential wells configured to change the depth corresponding to the magnitude of the physical or chemical quantity, to inject electric charges into these potential wells, and to convert the physical or chemical amount to electric charges corresponding to the depth of the potential wells.

By this configuration, it is possible to simultaneously measure phenomena at a plurality of different positions. Because the physical or chemical quantity is converted into electric charges, it is possible to easily visualize the one-dimensional distribution or two-dimensional distribution of physical or chemical phenomena by using CCD (charge coupled device).

Further details, objects and advantages of the present invention will become apparent from the following description when taken in conjunction with the drawings, in which:

Fig. 1 is an illustration showing the basic construction of the equipment for measuring physical phenomena or chemical phenomena of this invention;

Fig. 2 is an illustration schematically showing the principal portion of the equipment;

Fig. 3 is an illustration for explaining the measuring principle of the equipment;

Fig. 4 is an illustration for explaining other measuring principle;

Fig. 5 is an illustration showing one example of the source follower circuit connected to the above-mentioned equipment;

Fig. 6 is a longitudinal cross-sectional view schematically showing the equipment according to the first embodiment;

Fig. 7 is a plan view schematically showing the construction of the principal portion of the above-mentioned equipment;

Fig. 8 is a longitudinal cross-sectional view showing one example of the sensor portion of the above-mentioned equipment;

Fig. 9 is a longitudinal cross-sectional view showing the other example of the sensor portion of the above-mentioned equipment;

Fig. 10 shows one example of the electric charge transfer section of the above-mentioned equipment, and (A) is a longitudinal cross-sectional view and (B) a plan view;

Fig. 11 is a CCD drive potential diagram of the above-mentioned electric charge transfer section;

Fig. 12 is a timing chart of CCD drive voltage of the above-mentioned electric charge transfer section;

FIG. 13 is a diagram showing the characteristics of the source follower circuit;

FIG. 14 is a diagram showing signals of each section of the above-mentioned source follower circuit;

FIG. 15 is a diagram showing one example of the manufacturing process of the equipment according to the first embodiment together with FIG. 16;

FIG. 16 is a diagram showing one example of the manufacturing process of the equipment according to the first embodiment together with FIG. 15;

FIG. 17 is a longitudinal cross-sectional view schematically showing the equipment according to the second embodiment;

FIG. 18 is an illustration for schematically illustrating the measuring principle of the two-dimensional magnetic field distribution;

FIG. 19 is an illustration schematically showing the equipment according to the third embodiment, and (A) is a longitudinal cross-sectional view and (B) a plan view;

FIG. 20 is a longitudinal cross-sectional view schematically showing the equipment according to the fourth embodiment;

FIG. 21 is an illustration showing another embodiment; and

FIG. 22 is an illustration showing still another embodiment.

Referring now to the drawings, preferred embodiments according to the invention will be described in detail hereinafter. First of all, FIG. 1 shows a basic construction of the equipment 1 for measuring physical phenomena or chemical phenomena according to this invention, and in this figure, numeral 2 denotes a semiconductor substrate comprising, for example, p type Si (silicon) which is about 500 μm thick.

To the semiconductor substrate 2, channel stoppers 3, an electric charge feeder section 4, electric

charge injection controller section 5, sensing section 6 as electric charge converting section, barrier section 7, electric charge transfer section 8, floating diffusion 9, reset gate 10, reset drain 11, and output transistor of MOS structure 12 are formed.

A sensor section 13 is formed by members of the electric charge feeder section 4, electric charge injection controller section 5, sensing section 6, and barrier section 7, and the sensing section 6 comprises potential wells configured to change the depth in accord with the magnitude of the physical or chemical quantity as later discussed. An output section 14 is formed by members of the floating diffusion 9, reset gate 10, reset drain 11, and output transistor 12.

By arraying the sensor section 13 two-dimensionally as shown in FIG. 7, data at a plurality of points are simultaneously taken in, and the signals at a plurality of points can be orderly processed by the electric charge transfer section 8 and the output section 14. The processing procedure will be later described in detail referring to embodiments. The sensor section 13 may be one-dimensionally arrayed.

FIG. 2 is an illustration schematically showing the plane configuration of the sensor section 13 and the portion connected to this, and in FIG. 2, numeral 5a denotes an electric charge injection controller section electrode, and 7a a barrier section electrode. Next description will be made on the measuring principle by the measuring equipment referring to the potential diagram shown in FIG. 3. In measurement, the pulse voltage is applied to the electric charge feeder section 4, barrier section 7, and reset gate 10, while direct current voltage is applied to other electrodes excluding the floating diffusion 9.

Now, in general, in the MOS structure using the p type semiconductor, it is known that applying the positive voltage to the metal electrode allows the depletion layer to form at the interface between the insulator and the semiconductor in accordance with the voltage. Therefore, using this phenomenon, as shown in FIG. 3, the potential condition is formed at the semiconductor-insulation film interface.

Under the condition 1, the potential of the electric charge feeder section 4 is set to a high level (higher in the arrow direction), and no electric charge 15 is injected to the sensing section 6.

Under the condition 2, as shown in FIG. 3 (B) electric charges 15a are charged into the sensing section 6 by lowering the potential of the electric charge feeder section 4.

Under the condition 3, as shown in FIG. 3 (C), electric charges 15a leveled off by the electric charge injection controller section 5 are accumulated in the sensing section 6 by raising the potential of the electric charge feeder section 4.

Under the condition 4, as shown in FIG. 3 (D) the electric charges 15a accumulated in the sensing section 6 are transferred to the floating diffusion 9 by raising the

potential of the barrier section 7.

Under the condition 5, as shown in FIG. 3 (E) the barrier section 7 is closed after all the electric charges 15a of the sensing section 6 are transferred to the floating diffusion 9 and flow-in of electric charges is stopped. Under this stage, the potential of the floating diffusion 9 is determined by the amount of transferred electric charges 15a, and this potential is inputted to the gate section of the output transistor 12 of the MOS structure, and the drain current of this output transistor 12 is measured with the source follower circuit 17 as shown in FIG. 5.

Under the condition 6, as shown in FIG. 3 (F), the reset gate 10 is turned on and reset to the potential of the reset drain 11 after the potential of the floating diffusion 9 is read. By this resetting, the condition returns to that same as the condition 1 again. That is, by repeating the operations of condition 1 to condition 6, electric charges can be outputted to the outside.

FIG. 4 shows the other embodiment of the measuring equipment, and in this measuring equipment, the first barrier section 7A, electric charge accumulation section 16, and the second barrier section 7B are provided after the sensing portion 6, and the electric charges 15b for several terms are accumulated at the electric charge accumulation section 16, and after a certain amount of electric charges is accumulated, the potential of the second barrier section 7B is raised, and the electric charges accumulated at the electric charge accumulation section 16 are transferred to the electric charge transfer section 8. In the measuring equipment configured in this way, the sensitivity becomes several times, and it is possible to carry out measurement at higher accuracy.

As understood from the explanation concerning FIG. 3 and FIG. 4, in this measuring equipment, there used is an electric charge conversion mechanism for forming potential wells (sensing section 6) configured to vary the depth in accordance with the magnitude of the physical or chemical quantity on the semiconductor substrate 2, injecting electric charges 15 to the potential wells 6, and converting the physical or chemical quantity to electric charges in accordance with the depth of these potential wells.

In the measuring equipment shown in FIG. 3 and FIG. 4, the potential of the electric charge feeder section 4 is raised and lowered to level off the electric charges accumulated at the sensing section 6, but in place of this configuration, it is allowed to hold the potential of the electric charge feeder section 4 constant, raise and lower the level of the electric charge injection controller section 5, and level off electric charges accumulated at the sensing section 6.

FIG. 5 shows one example of the source follower circuit 17, which comprises a resistor 18, output terminal 19, and grounding terminal 20, and the output signal in this circuit 17 greatly varies in accordance with the size of the resistor 18 connected as shown in FIG. 13

but linear voltage signals can be obtained with respect to the output current. Numeral 21 designates a monitor equipped with data processing capabilities or image processing capabilities connected to the output terminal 19.

Referring now to FIG. 6 and after, various measuring equipment with the electric load conversion mechanism built in will be explained.

10 [First Embodiment]

For the first embodiment, description will be made on an equipment for measuring the two-dimensional distribution of the pH of the solution. FIG. 6 schematically shows a two-dimensional distribution measuring equipment of pH of the solution, and in FIG. 6, numeral 22 is a substrate, the top surface of which a cell 24 for accommodating the sample 23 such as the solution is formed. This substrate 22 imparts water resisting property to the sample 23 by providing resin mold. Numeral 25 is a reference electrode immersed in the sample 23, and by applying a specified voltage across the substrate 22 by the direct current power supply 26, this reference electrode 25 brings the potential of the sample 23 to a specified high level with respect to the substrate 22. The applied voltage causes the sensing section 6 to be in the depleted condition.

In the pH two-dimensional distribution measuring equipment of the above-mentioned configuration, the outputted signals are inputted as they are to the image output unit 27 such as televisions, etc. to output images, or the output signals may be AD-converted to be inputted to the computer.

FIG. 7 schematically shows the configuration of the top surface of the substrate 22, which comprises a plurality of sensor sections 13 for converting the pH to electric charges, an electric charge transfer section 8 for transferring electric charges converted at the sensor section 13 in the arrow direction, and an output section 14 for converting the transferred electric charges into output signals. The electric charge section 8 comprises horizontal CCD 8H and vertical CCD 8V.

FIG. 8 shows the construction of the sensor section 13. This sensor section 13 is formed as follows. That is, the p type Si substrate 2 which is made to be the substrate 22 is thermal oxidized to form the oxide film (SiO₂) 28, and part of the oxide film is etched and further thermal oxidized to form the gate oxide film 29. The film thickness of this gate oxide film 29 is about 500 Å, and electrodes 30, 31 are formed by depositing low-resistance P-doped poly-silicon to the portions corresponding to the electric charge injection controller section 5 and the barrier section 7 on the top surface, respectively.

The film thickness of these electrodes 30, 31 is about 3000 Å, and the film is thermal oxidized to about 1000 Å after deposition. Thereafter, the P-doped low-resistance poly-silicon is deposited again and the elec-

trode 32 is formed on the top surface of the electric charge transferring section 8. The film of this electrode 32 is thermal oxidized to about 1000 Å after poly-silicon is deposited to the level similar to that of the electrodes 30, 31. Oxidizing the film in this way can hold insulation between electrodes. Thereafter, Si_3N_4 , (Ta_2O_5 or Al_2O_3 acceptable) is deposited to about 700 Å to form the sensing section 6. Numeral 33 designates an electrode formed with aluminum.

FIG. 9 shows the other embodiment of the sensor section 13, and in the sensor section 13 shown in FIG. 9, a reference electrode is incorporated. That is, in this sensor section 13, in place of the electrode 30 of the electric charge injection controller section 5 shown in FIG. 8, a film 34 non-sensitive to pH is installed. The threshold value of the sensing section 6 is adjusted and the potential wells of the sensing section 6 are made deeper as compared to the electric charge injection controller section 5. In order to achieve electric connections between the sample and the substrate, an electrode 35 comprising inert metal such as platinum, etc. is installed. The electric charge injection controller section 5 and the sensing section 6 are designed to allow the sensing section 6 only to respond to pH and not to allow the electric charge injection controller section 5 to respond, but both are equally subject to influences such as external noises or potential variations at interface between the electrode 35 and the sample. That is, the difference of potential between the electric charge injection controller section 5 and the sensing section 6 reflects the pH value. Consequently, injecting electric charges to the sensing section 6 can convert the pH value to electric charges.

Now description will be made on the width of the electrodes 30 to 33, 35 and the sensing section 6. First of all, because as for the electrodes 30 to 33, 35 the electric charge injection controller section 5 is portions that serve to allow the electric charges fed from the electric charge feeder section 4 to be leveled off by the sensing section 6, about 10 µm would be enough for their width. The barrier section 7 only works to prevent electric charges leveled off by the sensing section 6 from flowing into the electric charge transferring section 8 readily, and about 10 µm would be enough for the width.

For the sensing section 6, because a certain amount of electric charge amount to be leveled off is required in order to improve the measuring accuracy, the minimum required area is secured for the purpose, and it has a size about some 10 µm x some 10 µm to 100 µm x 100 µm. For the size of this sensing section 6, various sizes are set with the electric charge transferring section 8 and the floating diffusion 9 taken into account. Experimentally, the sizes of the sensing section 6, electric charge transferring section 8, and floating diffusion 9 were designed to be 100 µm x 100 µm, 50 µm x 200 µm, 21000 µm², respectively, and measurement was carried out, and in the source follower circuit

— 17 using a 120 kΩ resistor 18 (see FIG. 5), about 80 mV output signals have been obtained per 1 pH.

FIG. 10 shows one example of the configuration of the electric charge transferring section 8, and FIG. 10 (A) shows a cross-sectional structure and FIG. 10 (B) a top surface structure, respectively. The electric charge transferring section 8 shown in FIG. 10 comprises CCD of 4-phase structure, and by depositing P-doped low-resistance poly-silicon in two layers in about 3000 Å thickness on the top surface of the oxide film 29 to form four electrodes 36A, 36B, 36C, 36D. Each of the electrodes 36A to 36D are oxidized to about 1000 Å in order to achieve insulation from one another.

FIG. 11 and FIG. 12 are illustrations for explaining the drive principle of the electric charge transferring section 8, and in particular, FIG. 11 shows the CCD drive voltage of the electric charge transferring section 8, and FIG. 12 is a timing chart of the CCD driving voltage. Symbols Ø 1 to Ø 4 in FIGS 11, 12 and 13 correspond to 36A to 36D, respectively.

CCD drive in the electric charge transferring section 8 is not limited to the four phases, but one-phase drive, two-phase drive, etc. may be accepted, and suitably selected in accordance with the electric charge amount to be transferred. As the number of the sensor section 13 increases, the transfer efficiency causes big problems, but in such event, it is preferable to use a bulk channel with high transfer efficiency.

The electric charge transferred by the electric charge transferring section 8 is transferred to the floating diffusion 9 (see FIG. 7) of the output section 14, and varies the potential of the floating diffusion 9. This potential variation is inputted to the gate of the output transistor 12, and the drain current of the output transistor 12 is read by the source follower circuit 17 (see FIG. 5).

FIG. 13 shows characteristics of the source follower circuit 17, and this data is obtained when the MOS transistor of 200 µm in channel width and 50 µm in channel length is used for an output transistor 12 and the resistor 18 is set to various values. FIG. 13 indicates that by changing the value of the resistor 18 in the source follower circuit 17, the output value of the source follower circuit 17 is considerably changed.

Now, in measuring the pH, to improve the measuring accuracy, a large change of output should be obtained with respect to the change in the amount of electric charges transferred to the floating diffusion 9. To achieve this, the area of the floating diffusion 9 should be made as small as possible, but excessively small area is easily saturated when incoming electric charges are excessively many and measurement is unable to be carried out. Consequently, it is preferable to determine the area of the floating diffusion 9 and the resistance 18 in the source follower circuit 17 by the area of the sensing section 6 as well as drive voltage of the electric charge transferring section 8.

FIG. 14 shows the output signal pulse of the source

follower circuit 17 together with the output gate pulse and the reset gate pulse, and the output signal pulse is outputted in a complicated form as shown in FIG. 14, but the true signal is the portion shown with symbol IV in the figure. That is, the portion of symbol I is the pulse signal generated when the reset gate is turned on, and is the signal generated as long as the reset gate 10 is superimposed on the floating diffusion 9. The portion of symbol II is the signal under the electrically floating condition after the floating diffusion 9 is reset. The signal of symbol III is the pulse signal generated when the output gate is turned on.

The signal expressed by symbol IV is the signal when the output gate closes and all the electric charges transferred flow into the floating diffusion 9, and the signal at this timing becomes the true signal. This signal IV is transformed into the output signal consisting of the true signal only by using the sample and hold circuit (not illustrated), and is outputted to the outside. This external output is inputted to the monitor 27 (see FIG. 6) and visualized.

Referring now to FIG. 15 and FIG. 16, the manufacturing process of the two-dimensional pH distribution measuring equipment is described. This process is only one example, and the device fabricated by this process uses an electric charge transferring system of the surface channel.

(1) First of all, a p-type Si wafer 41 of about $10 \Omega\text{cm}$ resistivity is wet-oxidized at 1100°C for about 90 minutes using a thermal oxidation furnace, and oxide film (field oxide) 42 of about 6000 \AA is formed on both top and bottom surfaces (see FIG. 15 (A)).

(2) Then, channel stoppers 3 are formed (see FIG. 15 (B)). The method for forming the channel stopper 3 is to etch the field oxide 42 at the stopper forming places using hydrofluoric acid (HF) and to diffuse boron (B) at the places. The method for diffusing boron is, for example, to form by predeposition a solid diffusion source at 1100°C for 15 minutes together with the wafer 41, then, after removing the borosilicate glass, to drive-in oxidize at 1140°C for about 1 hour, and then, to anneal in the nitrogen gas atmosphere for about 10 minutes.

(3) The electric charge feeder section 4, floating diffusion 9, and the source and the drain of the output transistor 12 are n-type diffusion regions (see FIG. 15 (C)), and these are formed in the same manner as in the case of channel stoppers 3 with the exception that the liquid phosphorous diffusion source is used for a diffusion source, and are formed in order of predeposition, drive-in oxidation, and annealing.

(4) The electric charge injection controller section 5, sensing section 6, barrier section 7, and electric charge transferring section 8 must have the oxide

film made thinner in order to allow the potential of the electrodes to exert great influences on the oxide film and the semiconductor interface. Consequently, as shown in FIG. 15 (D) the field oxide 42 corresponding to these sections are etched with hydrofluoric acid, and then, it is oxidized at 1050°C for about 2.5 hours, and annealed for about 20 minutes in the nitrogen gas atmosphere to form the gate oxide 43 in thickness of about 1000 \AA .

(5) For the electrode, as already described, the P-doped low-resistance poly-silicon is used. First of all, using CVD, P-doped low-resistance poly-silicon is deposited to about 3000 \AA . Using a photo-lithography, poly-silicon other than the electrode forming portions is etched with a reactive ion etching machine. Thereafter, poly-silicon is oxidized at 1140°C for about 45 minutes to cover the poly-silicon electrodes 44 at the electrode forming portions with the oxide film 45 at about 1000 \AA (see FIG. 15 (E)). The oxide film 45 is provided for insulating from the other poly-silicon electrode 46 formed by depositing an additional poly-silicon film in the next process (see FIG. 16 (A)).

(6) Then, poly-silicon is deposited in the similar process to the above, and electrodes 46 are formed by carrying out patterning, and the poly-silicon electrode 46 are further covered with the oxide film 47 (see FIG. 16 (A)). This oxide film 47 is to successfully affix the nitride film (Si_3N_4) 48 in the subsequent process (see FIG. 16 (C)).

(7) Now, the oxide film 43 at the portion where the sensing section 6 is formed is degraded after passing various processes after gate oxidation. Therefore, this oxide film 43 is removed by the use of hydrofluoric acid and the gate oxide 43A of about 1000 \AA is newly formed (see FIG. 16 (B)).

(8) In order to provide pH sensitivity and water resisting property, the nitride film 48 is deposited to about 800 \AA using CVD (see FIG. 16 (C)).

(9) Contact holes 49 are opened so that voltage can be applied from the outside to each of the electrodes and n-diffused layers, respectively (see FIG. 16 (D)).

(10) In order to deposit aluminum to about $1 \mu\text{m}$ to form electrodes 50 at the portions where contact holes 49 are formed, electrode patterns are formed by photo-lithography, and portions other than these portions are etched (see FIG. 16 (E)).

In the above fabrication method, since the surface channel is employed in which the electric charge transfer takes place at the semiconductor 41 surface, the

transfer efficiency was about 98%, but as the number of pixels increases, the transfer loss becomes a problem. Therefore, when the number of pixels increases, it is preferable to use the bulk channel system in which electric charge transfer takes place inside the semiconductor 41.

According to the pH two-dimensional distribution measuring equipment of the above-configuration, the pH at a plurality of positions of different solutions can be simultaneously measured. Since the pH simultaneously measured is converted to electric charges, the two-dimensional distribution of pH can be easily visualized by transferring the electric charges using the techniques such as CCD.

In the above-mentioned embodiment, two-dimensional distribution of pH was intended to be measured, but by chemical modifying the surface of the sensing section 6 with suitable sensitive material, the ion concentration other than pH can be measured. That is, this invention can be suitably and extensively used for two-dimensional distribution measurement of ion concentration of samples, such as solutions, as well as applied to the following fields.

① Applicable fields as chemical microscope

- Chemical: ion concentration measurement
- Electro-chemical field, gas distribution measurement field
- Two-dimensional observation and analysis of titration

② Environment measurement

- Environment: application to bioremediation

③ Food inspection

- Foods, microorganisms

④ ME field

- Medical and ecological tissues: surface ion concentration measurement, cell surface potential measurement

⑤ Animal and plant field

- Plants: surface potential distribution measurement of callus
- Living being/front view animals

⑥ Corrosion measuring field

- Metal: painting and coating of metal corrosion

⑦ Surface analysis such as zeta potential, etc.

- • Zeta potential of powders and ceramics

The measurement subjects (samples) may be gas, liquid, solid, or powders, and the embodiment can be applied to chemical sensing which selectively reacts by the specific sensitive layer of the sensor section as well as to any phenomena in which electric particles fluctuate at the interface by physical contact, and for example, the distribution of liquid flow or the distribution of transient phenomena of instantaneous chemical reactions can be obtained in the form of high-sensitivity high-quality chemical images. In addition, the embodiment is useful from real-time visualization of titration phenomena to other kinds of analysis and display by image software.

15 [Second embodiment]

For the second embodiment, two-dimensional distribution measurement of pressure using a pressure sensor is described. FIG. 17 schematically shows one example of two-dimensional distribution measuring equipment of pressure, and in FIG. 17, numeral 60 designates a p-type Si substrate, 61 an N-well region of 1 μm or less formed at the surface of the substrate 60. Numeral 62 is a $\text{P}\pm$ diffusion layer formed in the N-well region 61, and is an emitter section doped at the concentration higher than that in the substrate 60. On this $\text{P}\pm$ diffusion layer 62, a thick oxide film which is about 1 μm thick is provided, and stress is focused on the emitter of this PNP transistor.

On the $\text{P}\pm$ diffusion layer 62, a contact hole is formed to install a metal electrode 63 to sweep up to the gate of the sensing section 64, and the potential of the $\text{P}\pm$ diffusion layer 62 is applied to the sensing section 64. The oxide film only of this sensing section 64 is made to be 1000 \AA thick, and the oxide film around it is made to be 5000 \AA thick. This is to greatly vary the potential in the vicinity of the interface between the semiconductor and the oxide film for the sensing section 64 only by the potential of the metal electrode 63. Numeral 65 designates channel stoppers formed surrounding the circumference of the sensing section 64, and potentially separate the sensing section 64 from the circumference. Numeral 66 is an insulator, and 67 is a power supply that biases in the reverse direction across the substrate 60, the collector, and the N-well region 61, the base. Though not illustrated, an electric charge feeder section, barrier section, etc. are provided perpendicular to the paper surface.

50 In the two-dimensional distribution measuring equipment of pressure, when mechanical stress 68 is exerted to the PNP transistor in the direction perpendicular to the PNP junction surface, voltage across the emitter and the base varies and the potential of the emitter section 62 varies. This potential change is swept to the sensing section 64 using the metal electrode. By this change of the swept potential, the potential at the interface between the oxide film and the semiconductor

of the sensing section 64 varies, and by injecting electric charges to it, the change in the potential is converted to the electric charge amount.

[Third embodiment]

For the third embodiment, a magnetic field two-dimensional distribution measuring equipment is explained. For this magnetic field measurement, the Hall effect is utilized. First of all, FIG. 18 is an illustration to schematically describing the measuring principle of the two-dimensional magnetic field distribution, and the insulating material 71 is accumulated on the top surface of the semiconductor substrate 70, and the semiconductor 72 is further accumulated on the top surface, and the current is allowed to flow in this semiconductor 72 in the arrow 73 direction. When the substrate 70 is set in such a manner that the magnetic field direction 74 crosses at right angles to the direction of the current 73 and is parallel to the substrate 70, voltage is generated in the direction perpendicular to the surface of the substrate 70. The two-dimensional distribution of the magnetic field can be measured by converting the magnitude of this voltage to electric charges by the above-mentioned electric charge conversion mechanism.

FIG. 19 schematically shows the construction of the sensor section of the magnetic field two-dimensional distribution measuring equipment configured on the basis of the measuring principle mentioned above, and FIG. 19 (A) shows a cross-sectional structure and FIG. 19 (B) a plane structure. In FIG. 19, numeral 74 designates a semiconductor substrate, 75 an electric charge feeder section, 76 an electric charge injection controller section, 77 a sensing section, 78 a barrier section, and 79 an electric charge transfer section.

And numeral 80 is an epitaxial grown Si layer deposited only on the top surface of the sensing section 77, 81 electrodes comprising poly-silicon, and 82 an insulation layer comprising an epitaxial grown Al_2O_3 insulation layer. The thickness of the Al_2O_3 layer is set to about 1000 Å at the bottom of the Si layer 80 and the poly-silicon electrodes 81, respectively, and is configured in such a manner that fluctuation of potential is positively generated.

Now, if the magnetic field is in the direction shown with the arrow mark 83, when the current is allowed to flow in the Si layer 80 as shown with the arrow mark 84, voltage by the magnetic field 83 is generated in the direction perpendicular to the semiconductor substrate 74, and the potential in the vicinity of the interface between the semiconductor 70 and the insulation layer 82 comprising Al_2O_3 fluctuates. The magnetic field two-dimensional distribution can be measured by converting this potential fluctuation into electric charges using the electric-charge conversion mechanism.

[Fourth embodiment]

For the fourth embodiment, the temperature two-dimensional distribution measuring equipment will be described. In this measuring equipment, the phenomenon in that the voltage across the emitter and the base of the PNP-transistor varies by the change of temperature is utilized, and this is nearly similar to the pressure two-dimensional distribution measuring equipment of the second embodiment (see FIG. 17) in this point. Consequently, in FIG. 20 that schematically shows the temperature two-dimensional distribution measuring equipment, like reference characters designate like or corresponding parts in FIG. 17. However, what is different is that temperature at a small area is given to the emitter 62 by bringing the metal 90 with good thermal conductivity in contact with the emitter 62. Therefore, by supplying the generated voltage to the sensing section 64 and converting it to electrical charges using the electric charge conversion mechanism, the temperature two-dimensional distribution can be measured.

Other physical phenomena or chemical phenomena, in almost all cases, can be converted to electrical signals such as voltage, current, etc., and converting these electrical signals to electric charges using the electric charge conversion mechanism, handling special to the electric charges can be achieved.

Each of the above-mentioned embodiments is intended to measure the two-dimensional distribution with respect to some specific physical phenomena or chemical phenomena by arraying the same sensor, but this invention shall not be limited to these, but by arraying a plurality of sensors of different kinds, a plurality of physical phenomena or chemical phenomena can be simultaneously measured.

For example, as shown in FIG. 21, by bringing and arranging a plurality of the sensor section 91 for measuring the pH and the sensor section 92 for measuring temperature closer to one another and transferring electric charges obtained by relevant sensor sections 91, 92 using independent electric charge transfer sections 93, 94, respectively, the two-dimensional distributions of pH and temperature can be obtained simultaneously.

As shown in FIG. 22, the electrode 96 is installed throughout the full surface of the top surface of the device 95 and a sample 97 (any of solid, liquid, or gas) is located in the form of sandwich between this electrode 96 and the device 95, and voltage is applied across the device 95 and the electrode 96 under this condition. By this contrivance, the sample with different resistivity 97 gives potentials varying at relevant positions to the device 95, and by converting this voltage to electric charges, it is possible to detect the two-dimensional distribution of the sample 97. By the way, numeral 98 designates the bias power supply.

According to the measuring method of the physical phenomena or chemical phenomena of this invention, phenomena in multiple different positions can be simul-

taneously detected. And since the physical or chemical quantity is converted to the electric charges, the two-dimensional distribution of the physical or the chemical phenomena can be easily visualized by the use of CCD. Depending on the data processing method, it is also possible to obtain the three-dimensional distribution. — 5

Because amplification of weak signals is possible by accumulating electric charges representing information of a plurality of points, it is possible to positively grasp microscopic changes of the phenomena. 10

Claims

1. A method of measuring physical phenomena or chemical phenomena comprising a process for injecting electrical charges into potential wells constructed to vary their depth in accordance with the magnitude of a physical or chemical quantity, and a process for converting the physical or chemical quantity into electric charges according to the depth 15 20 of the potential wells.
2. A method according to claim 1, wherein a potential of a sensing section (6) is changed for forming a potential condition in the vicinity of a semiconductor-insulation film interface. 25
3. An equipment for measuring physical phenomena or chemical phenomena comprising a plurality of potential wells constructed to vary their depth in accordance with the magnitude of a physical or chemical quantity and arrayed one-dimensionally or two-dimensionally, wherein electric charges are injected in these potential wells and the physical or chemical quantity is converted into electric charges 30 35 according to the depth of the potential wells.
4. An equipment according to claim 3, wherein a potential of a sensing section (4) is changed for forming a potential condition in the vicinity of a semiconductor-insulation film interface. 40

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Fig. 1

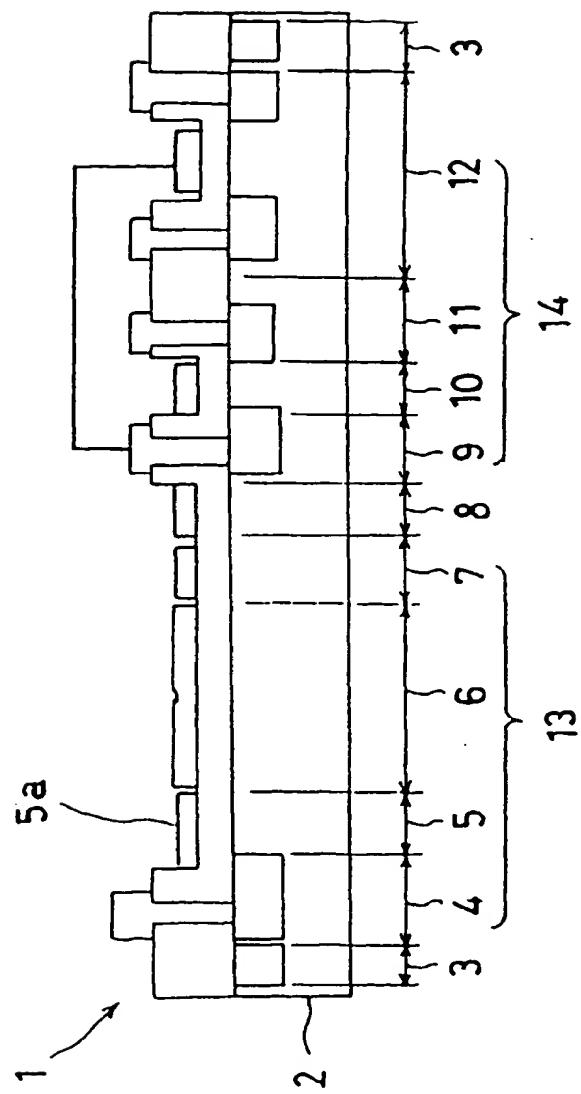


Fig. 2

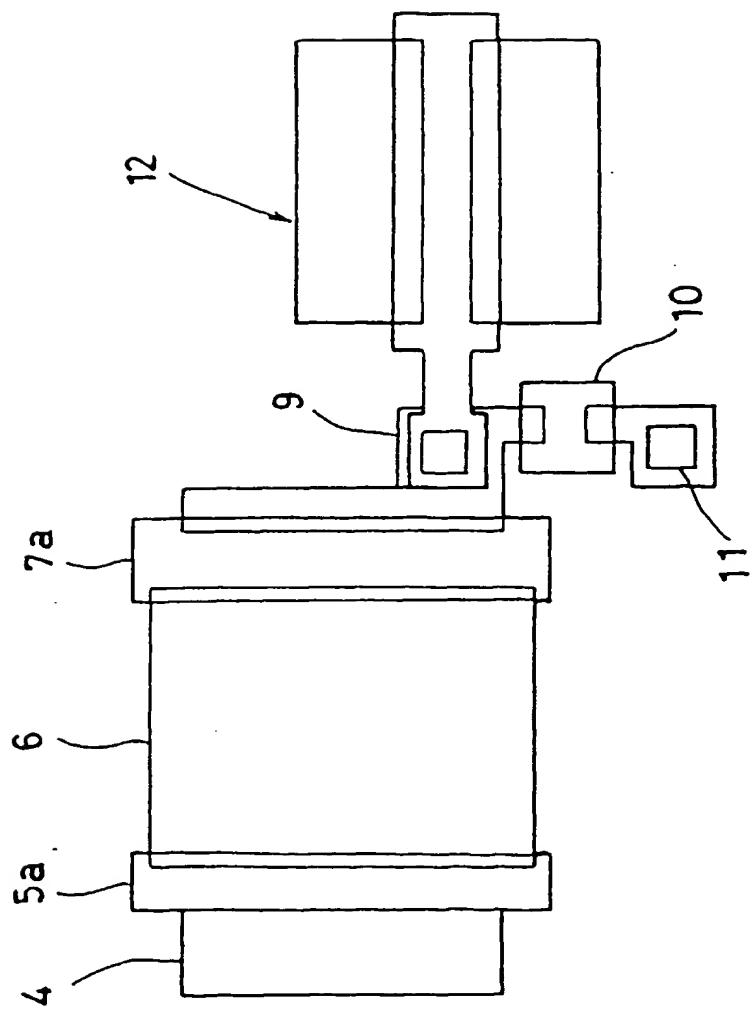


Fig. 3

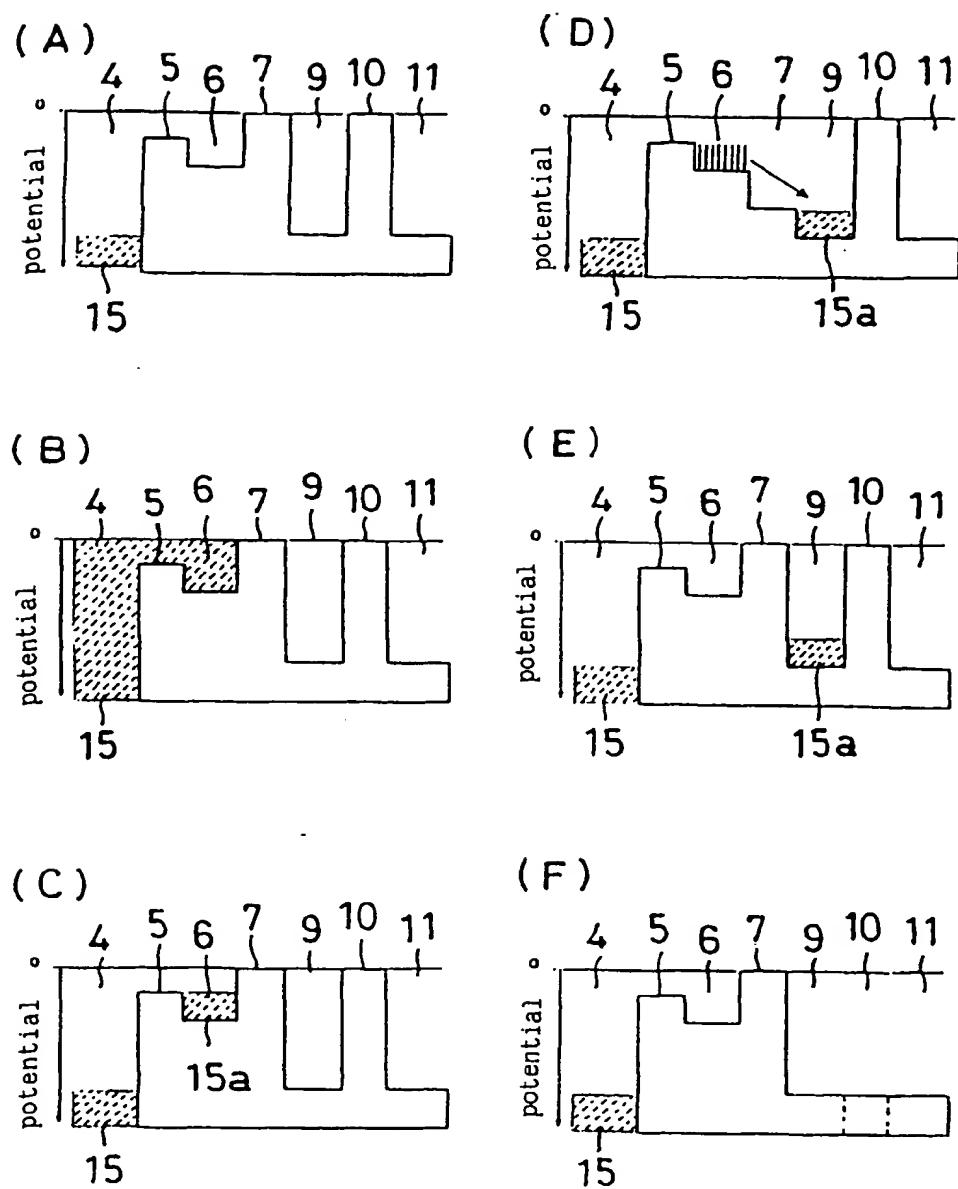


Fig. 4

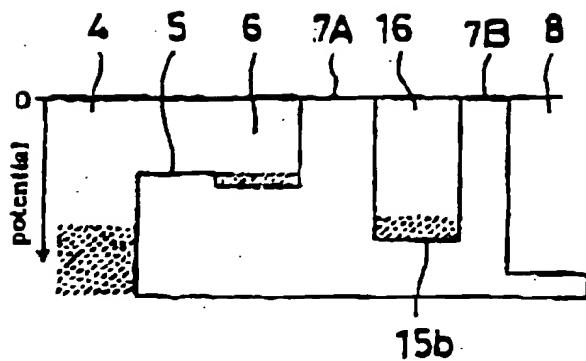


Fig. 5

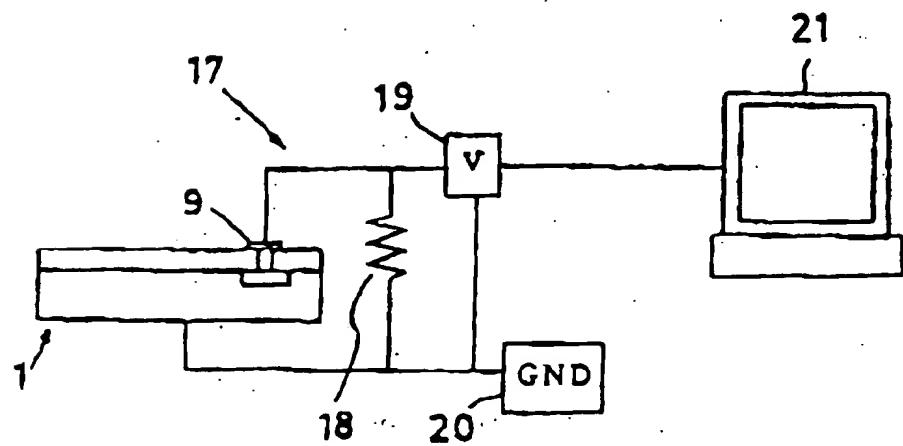


Fig. 6

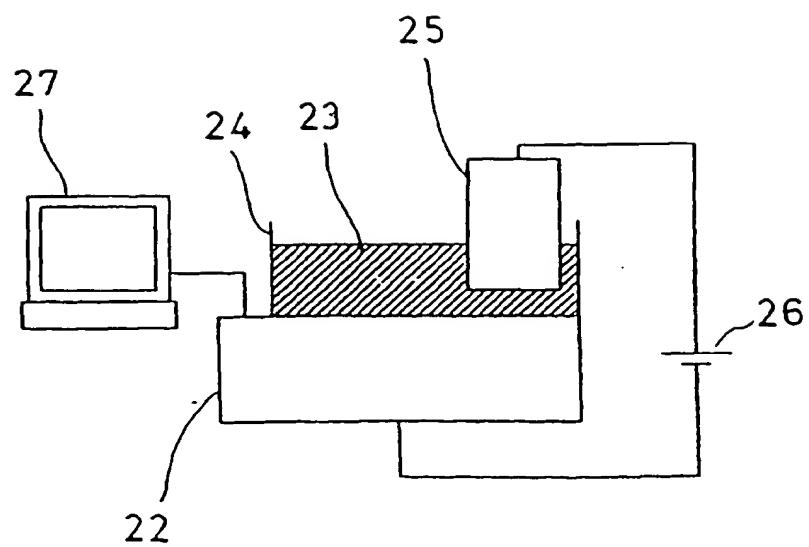


Fig. 7

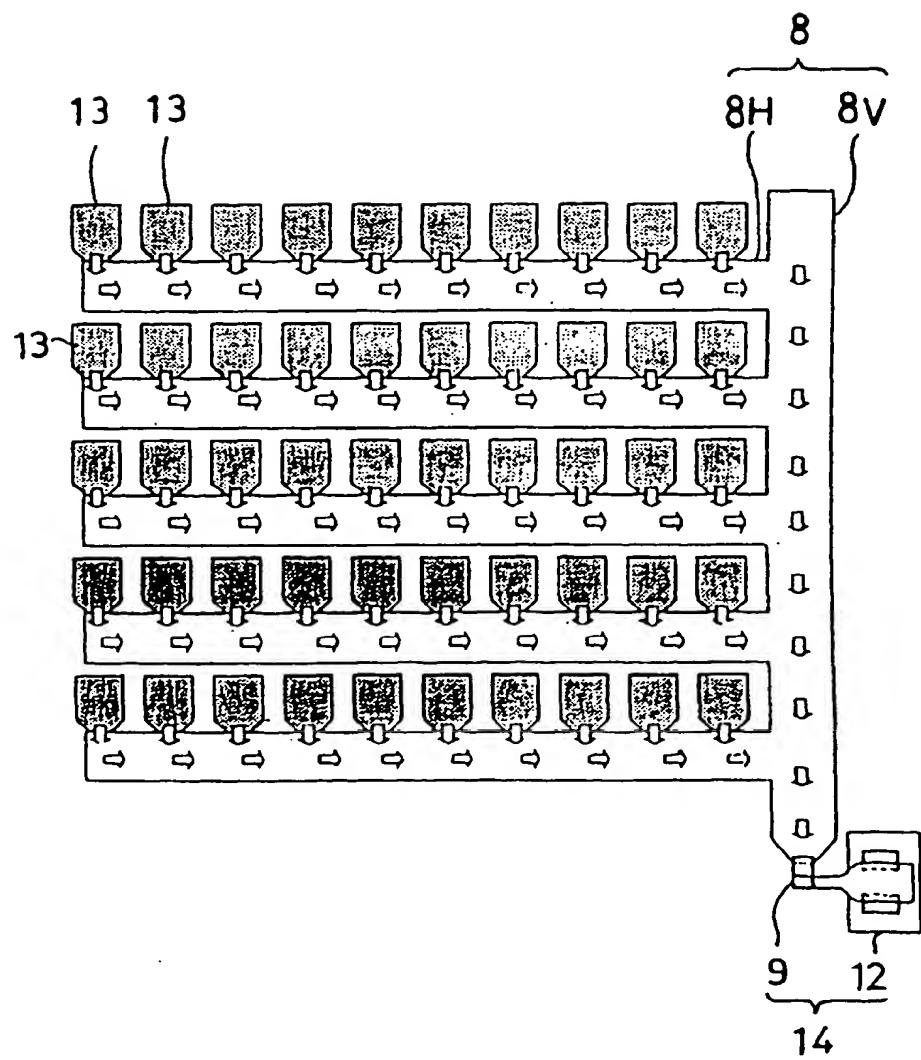


Fig.8

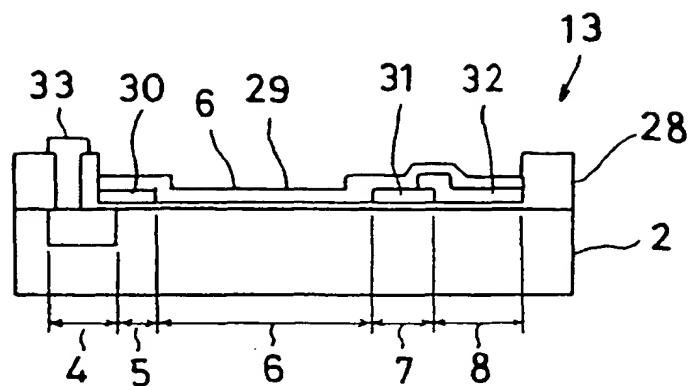


Fig.9

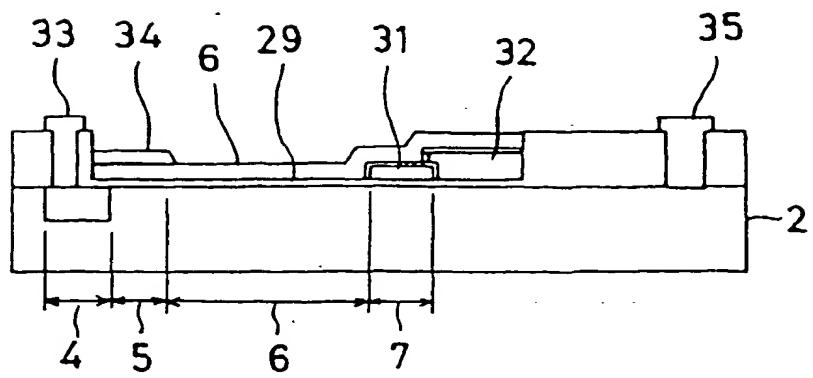
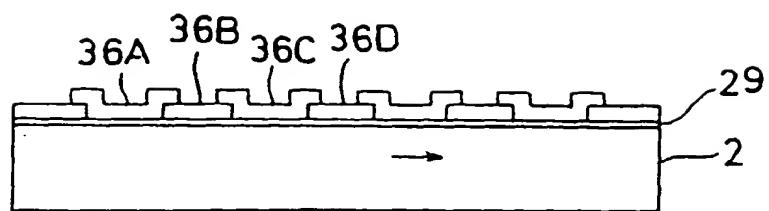


Fig.10

(A)



(B)

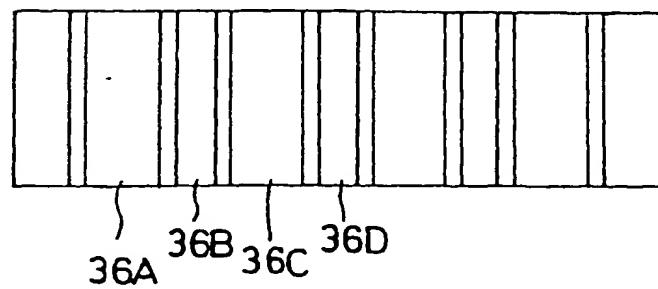


Fig. 11

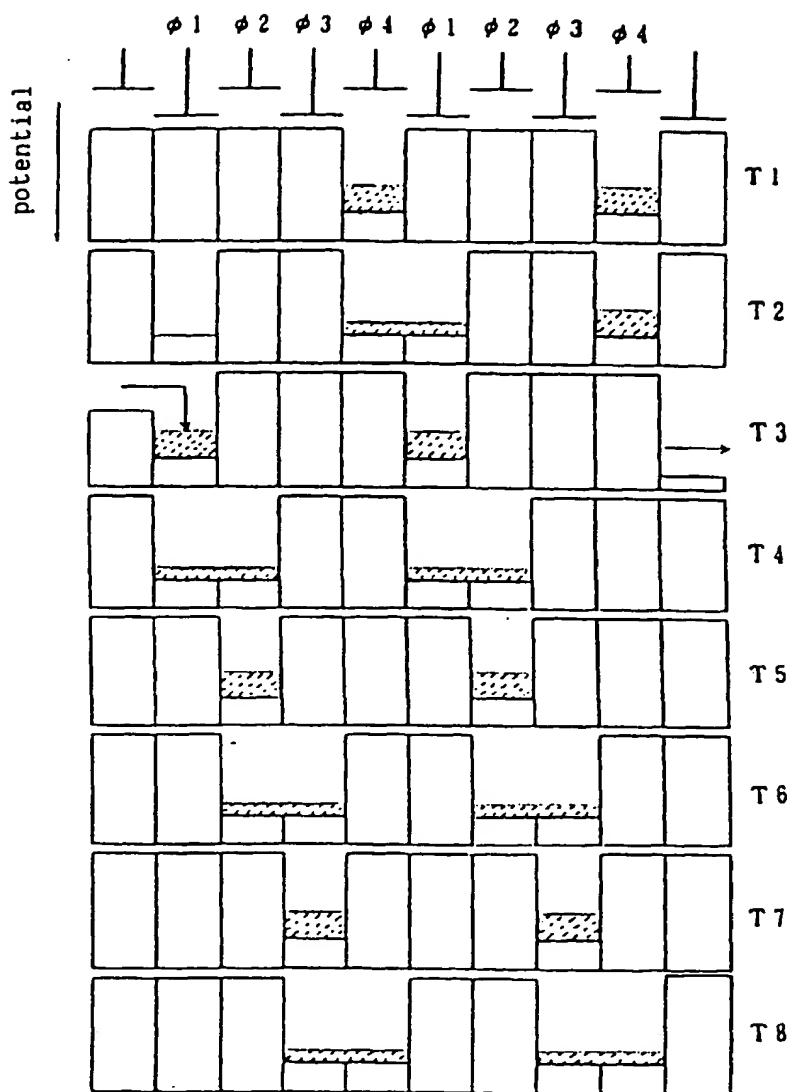


Fig. 12

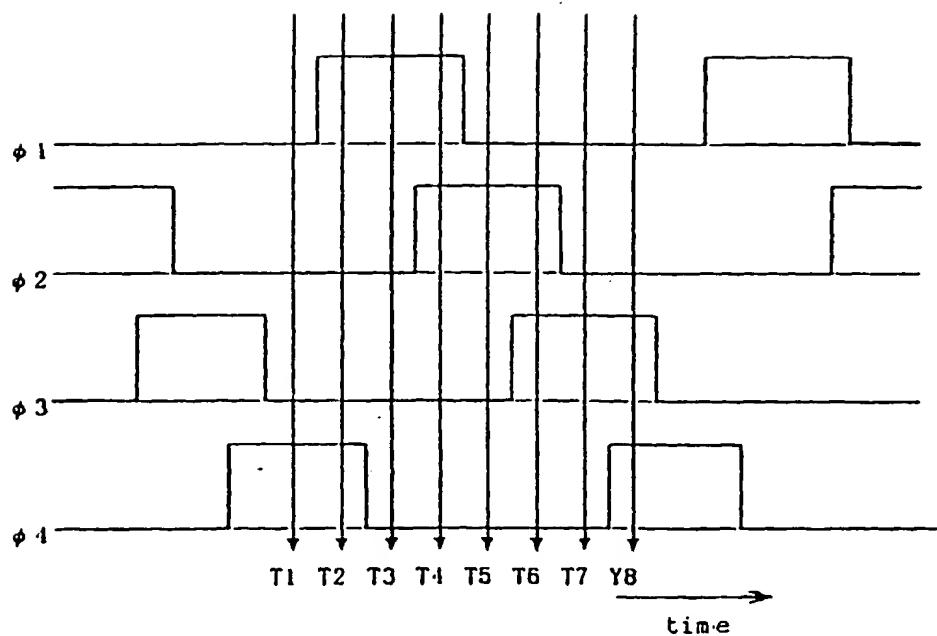


Fig. 13

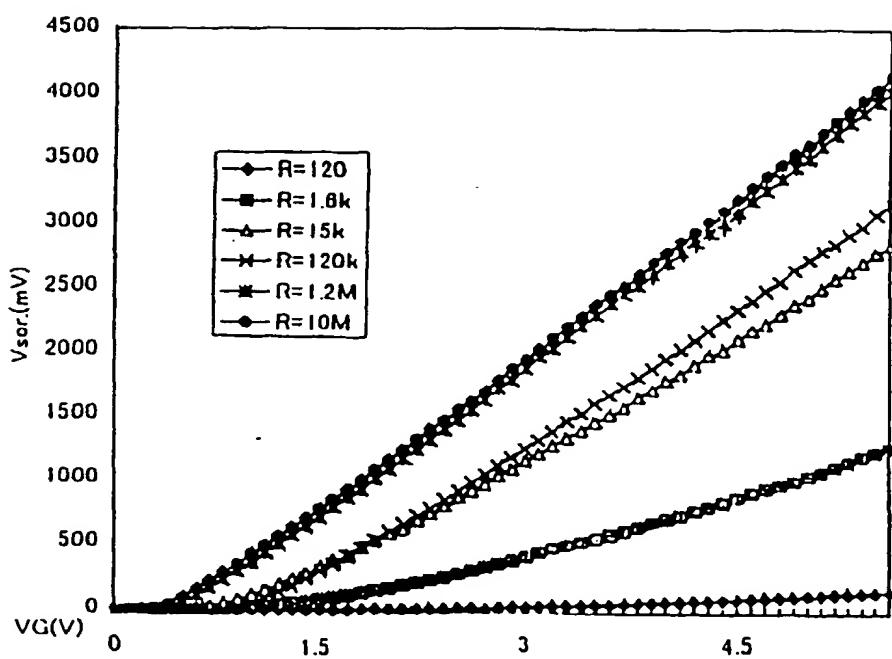


Fig. 14

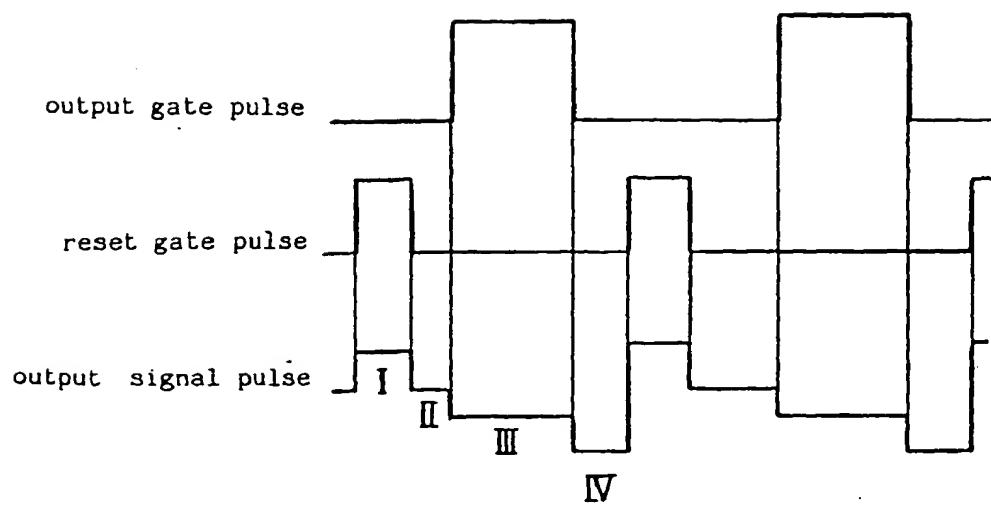
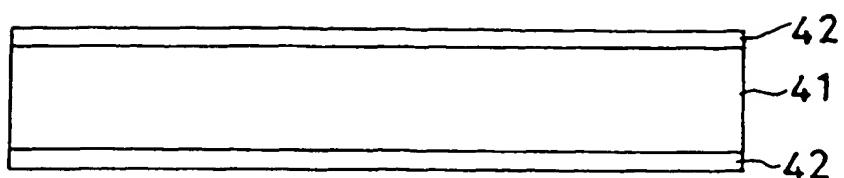
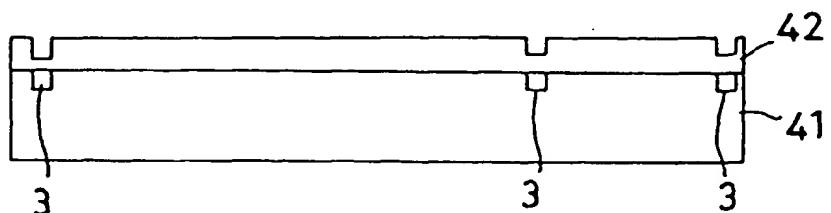


Fig. 15

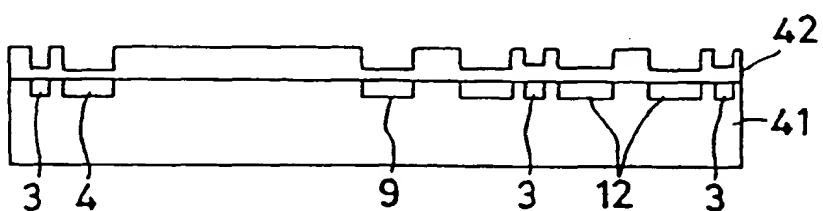
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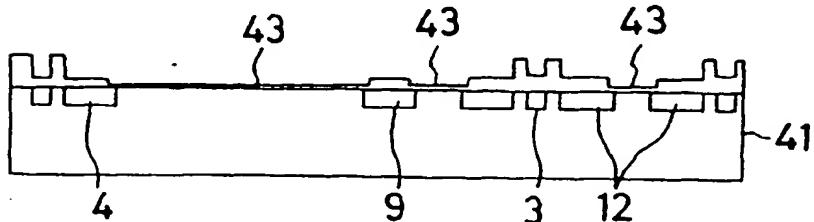
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(C)



(D)



(E)

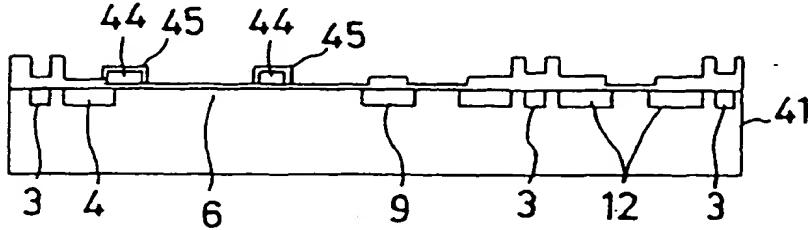


Fig. 16

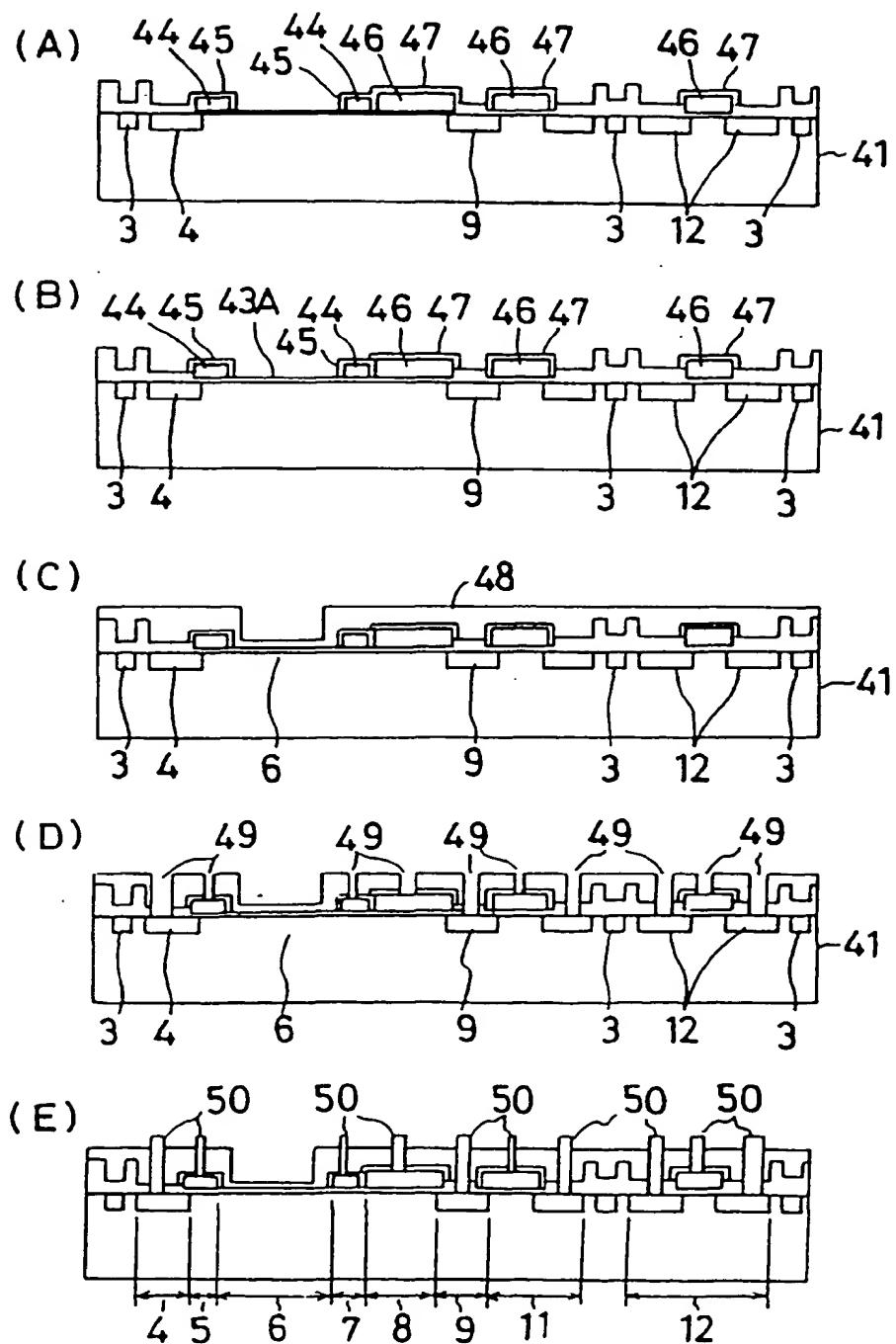


Fig. 17

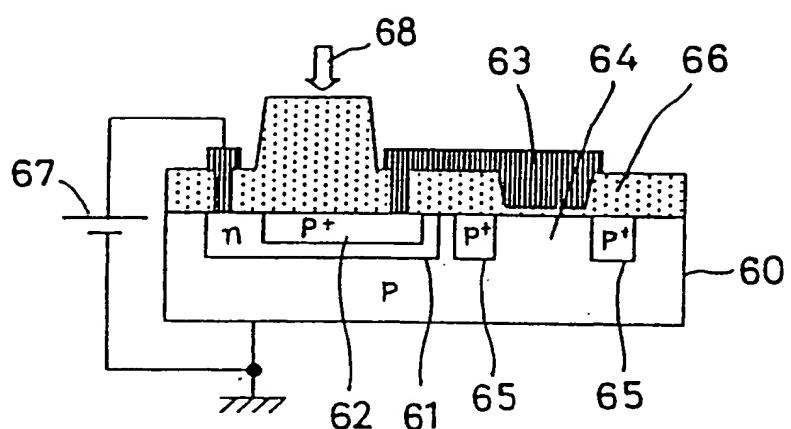


Fig. 18

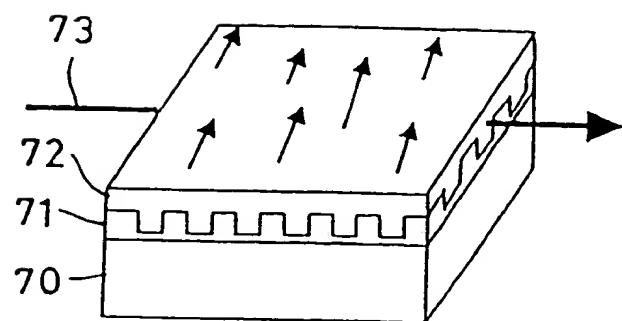


Fig. 19

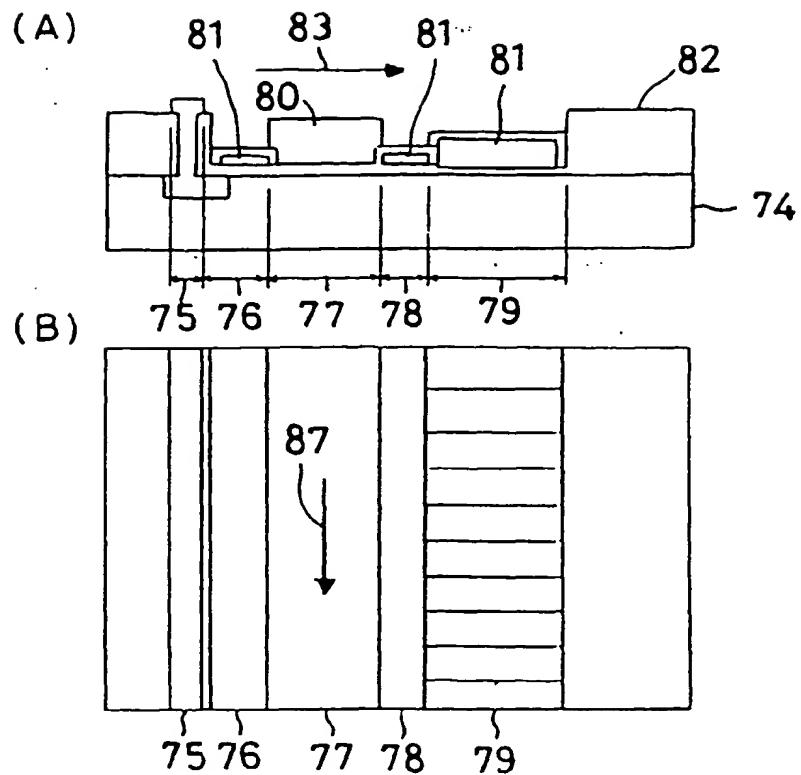


Fig. 20

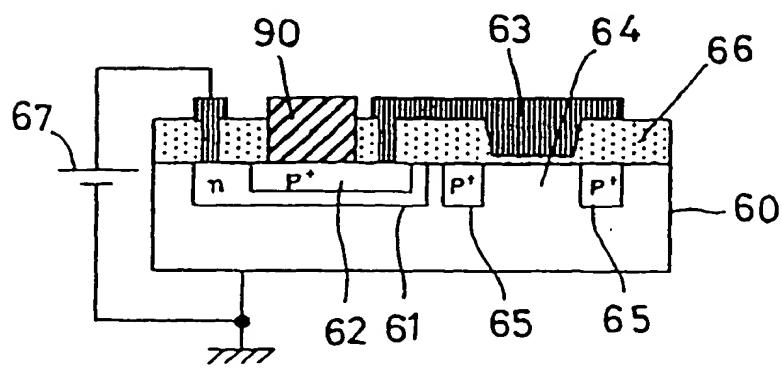


Fig. 21

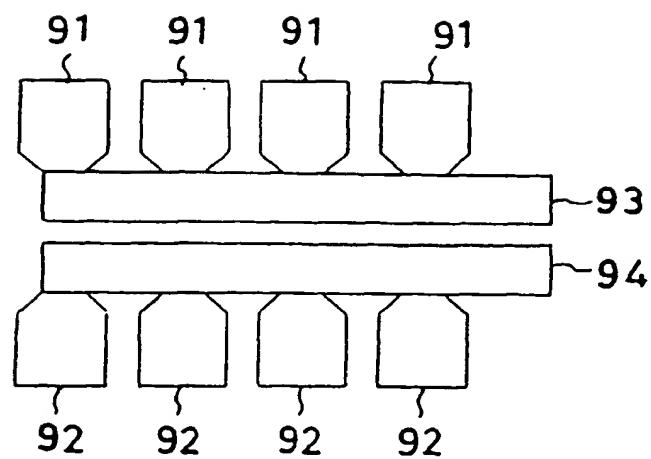
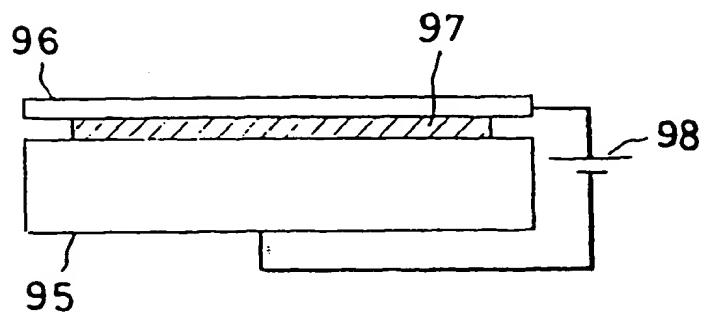


Fig. 22



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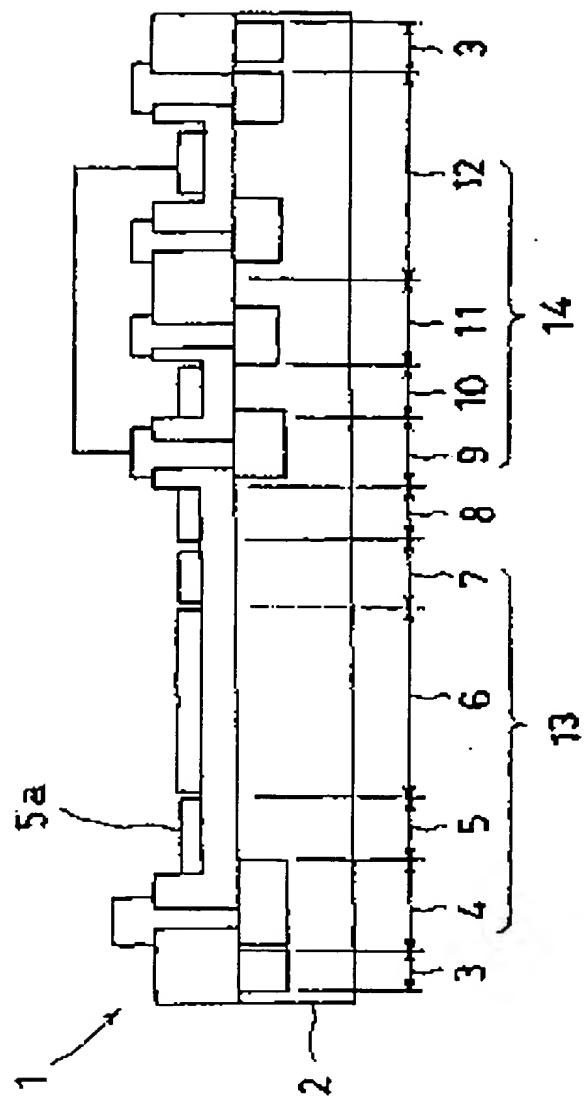


Fig. 2

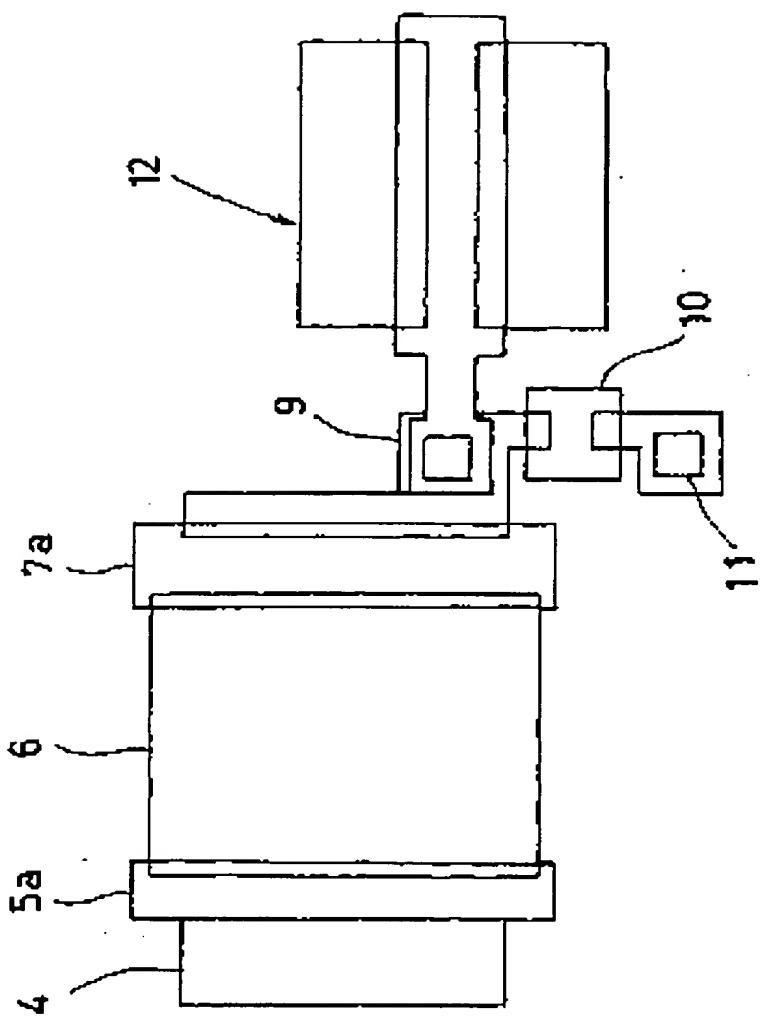


Fig. 3

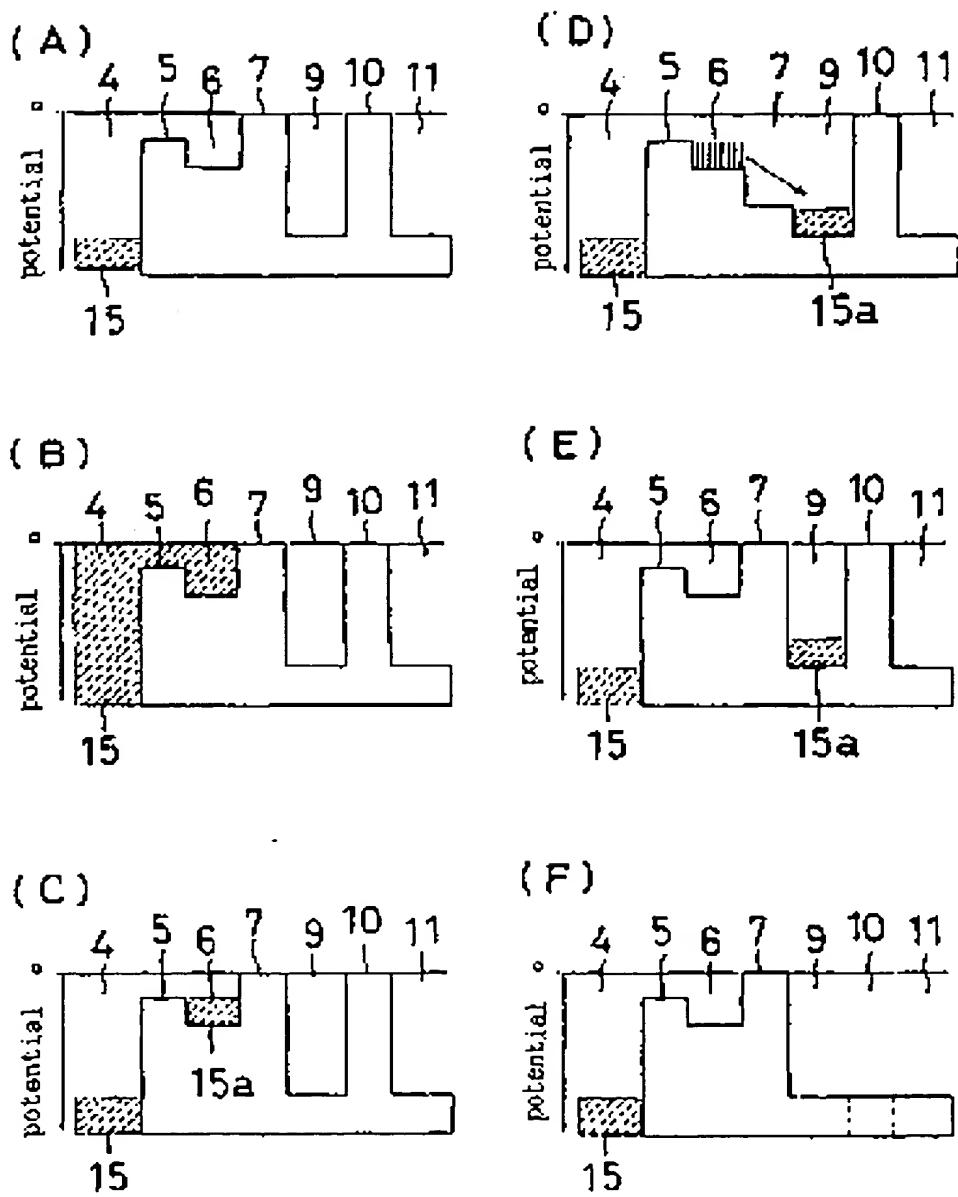


Fig. 4

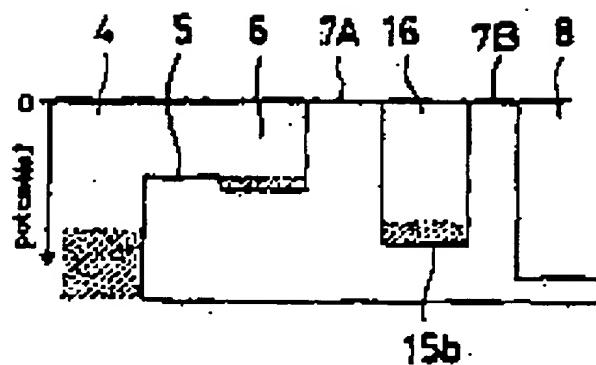


Fig. 5

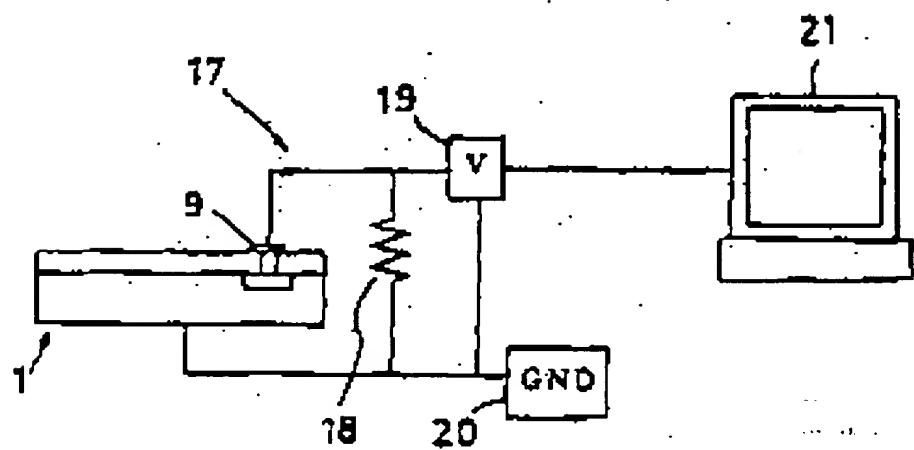


Fig.6

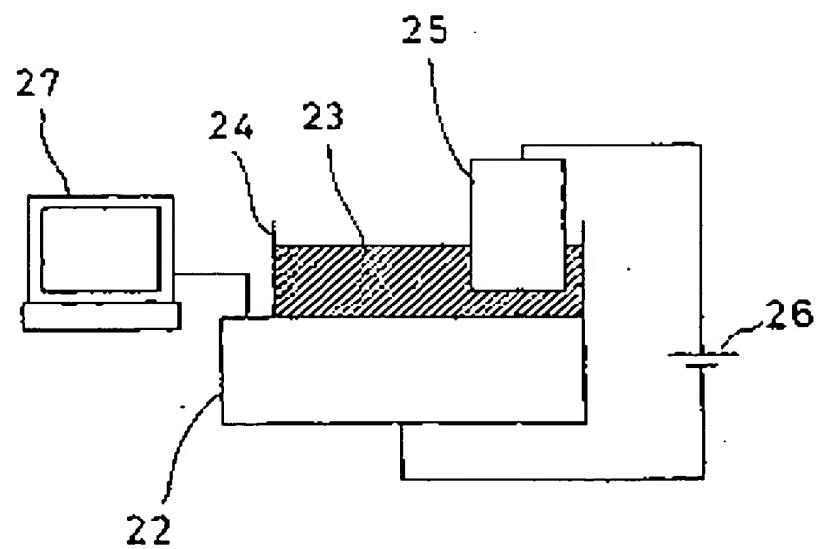


Fig. 7

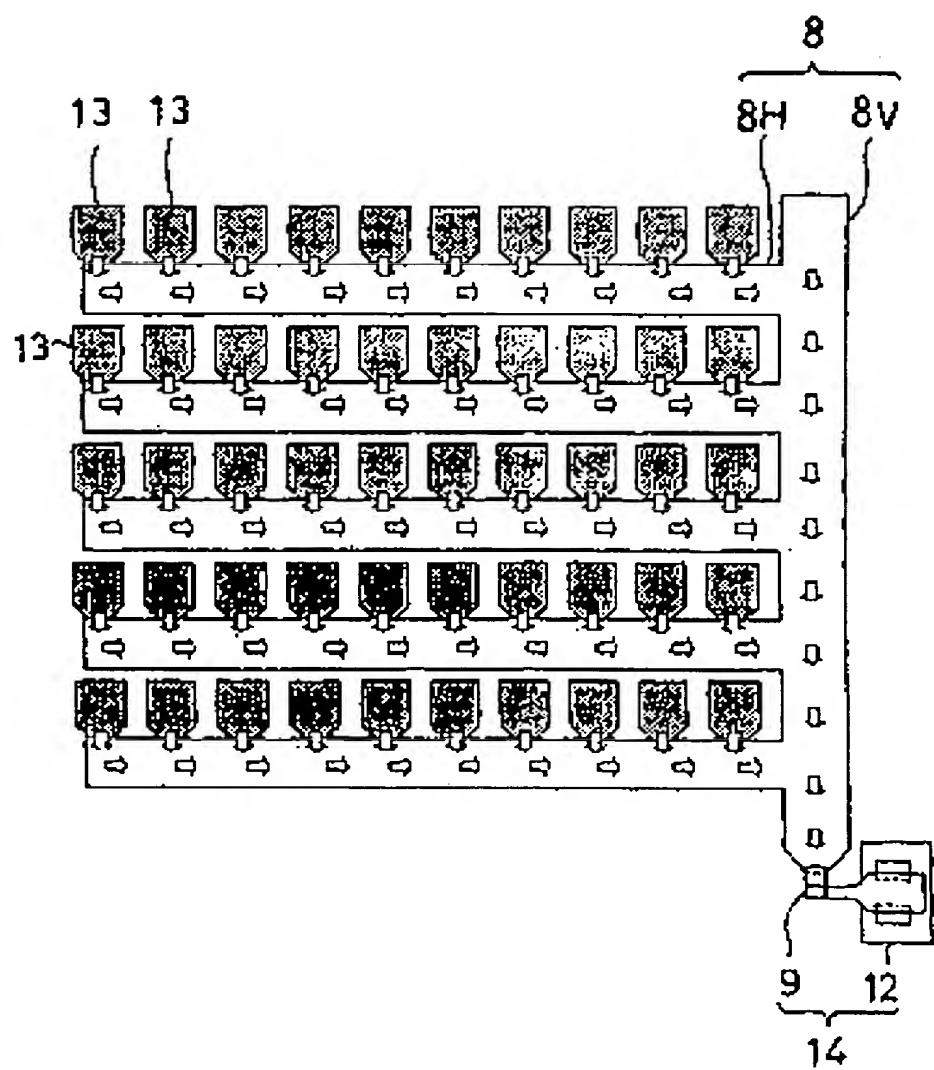


Fig. 8

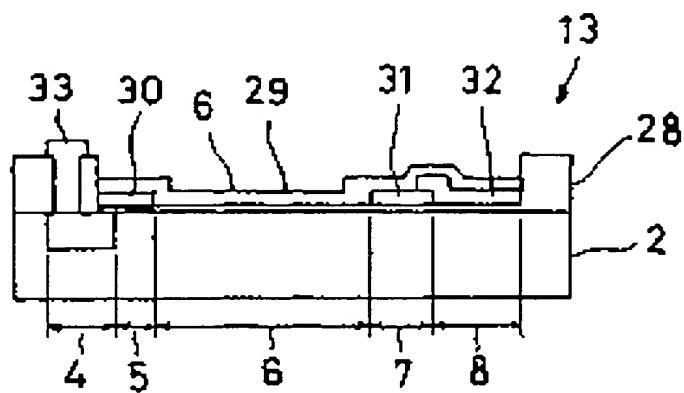


Fig. 9

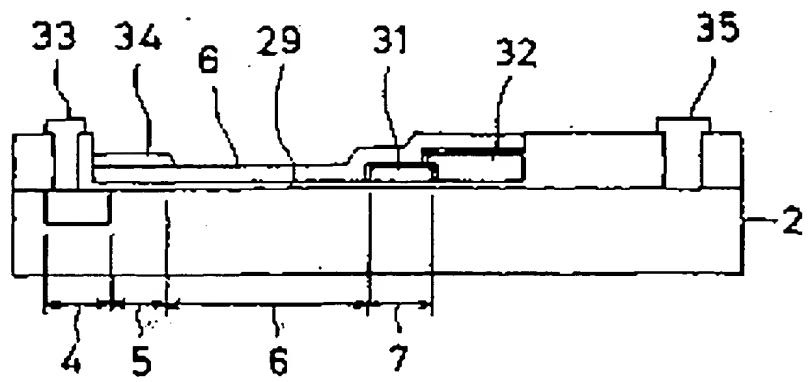
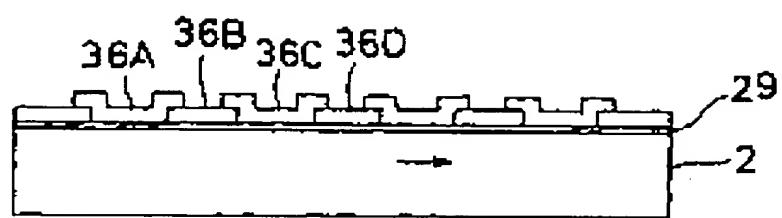


Fig. 10

(A)



(B)

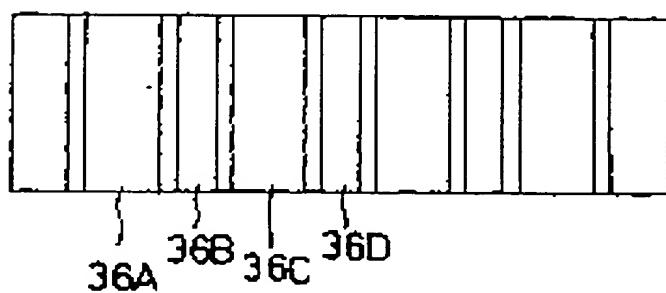


Fig. 11

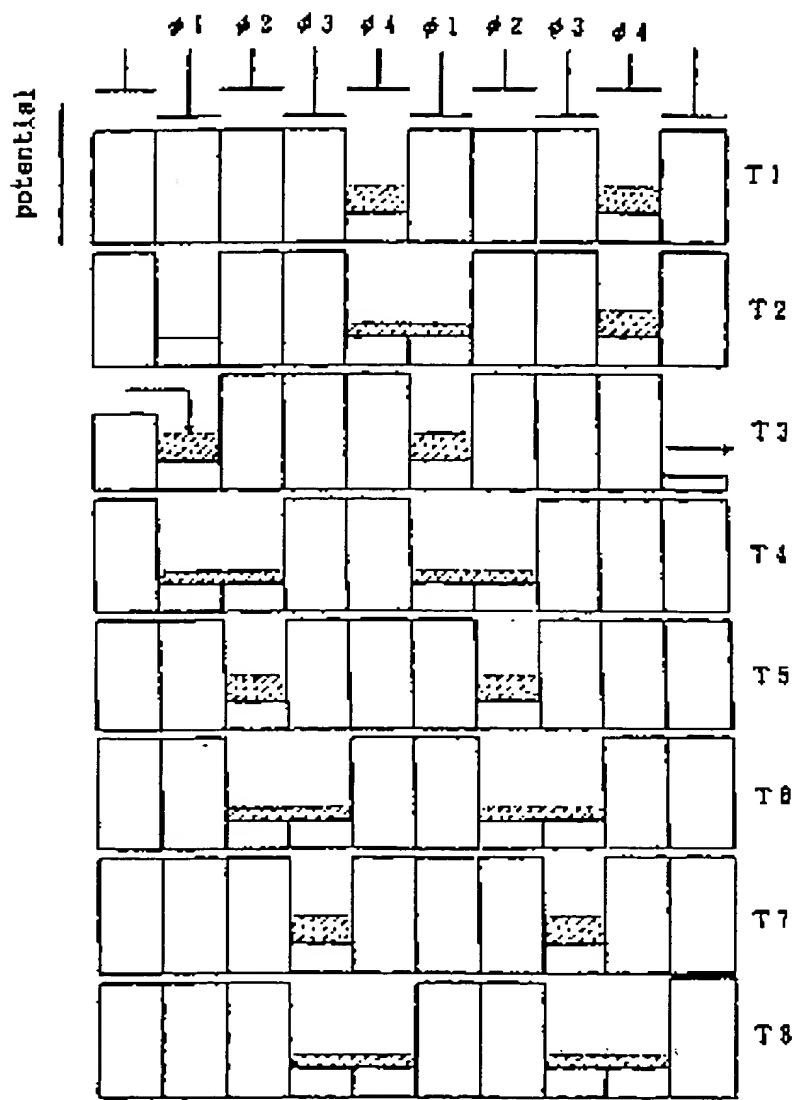


Fig. 12

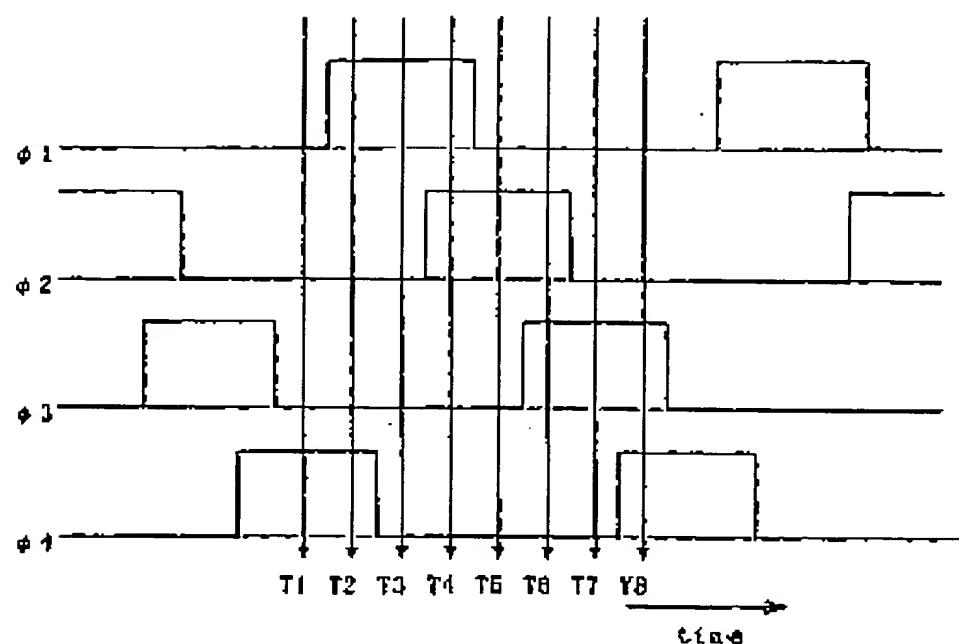


Fig. 13

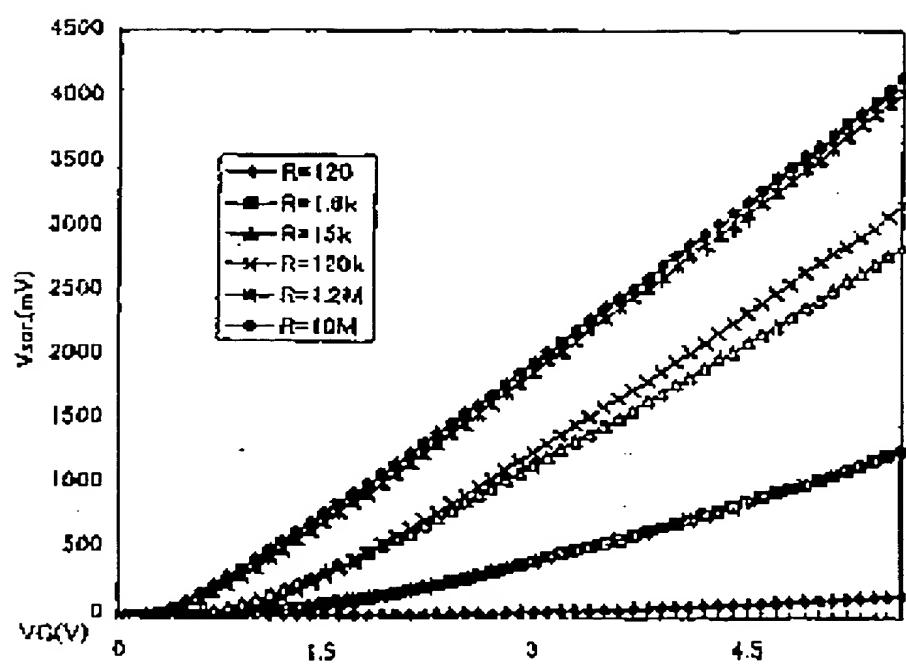


Fig. 14

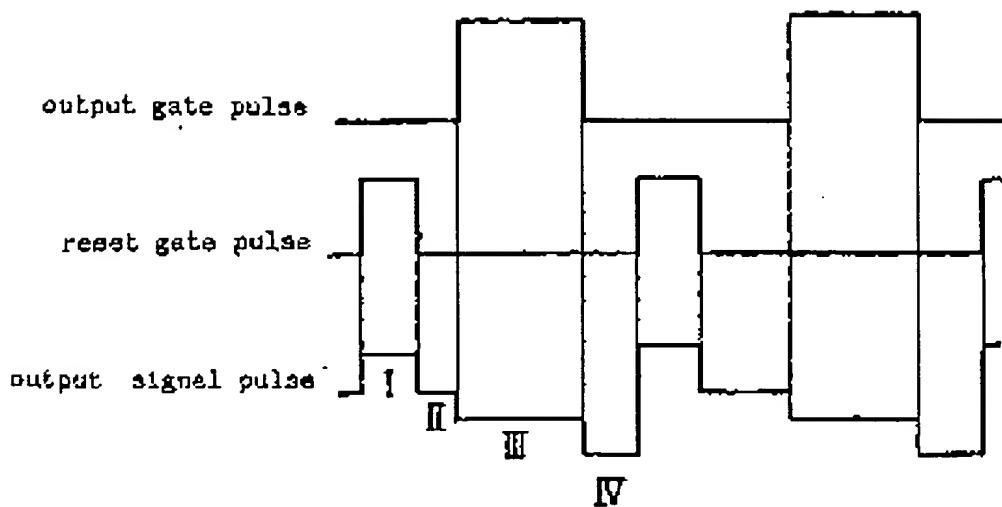
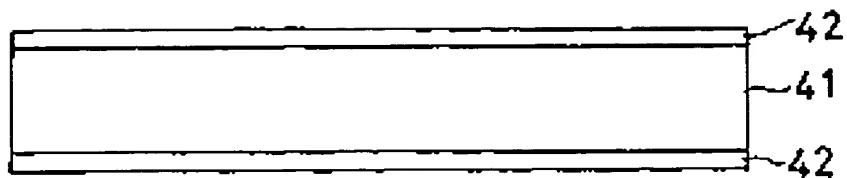
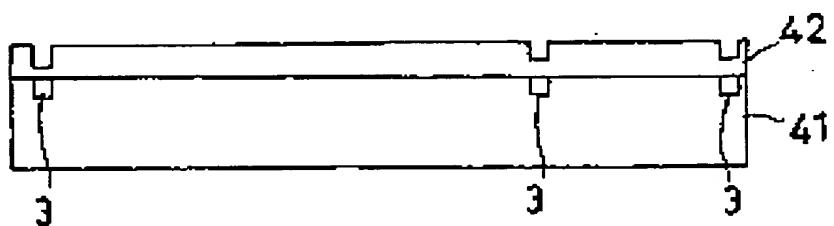


Fig. 15

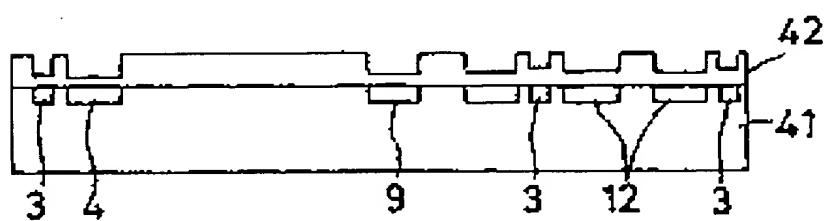
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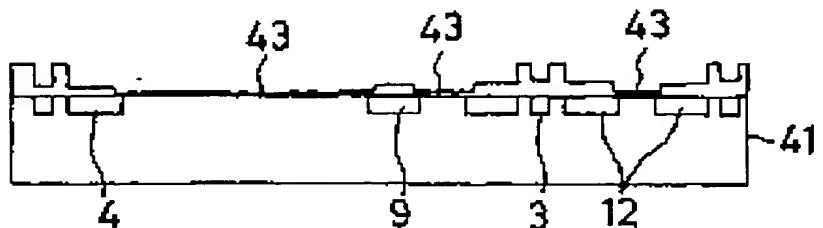
(B)



(C)



(D)



(E)

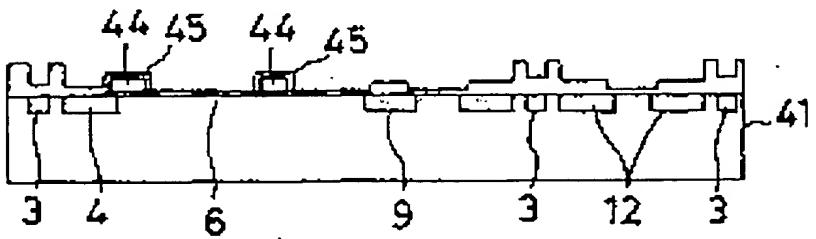


Fig. 16

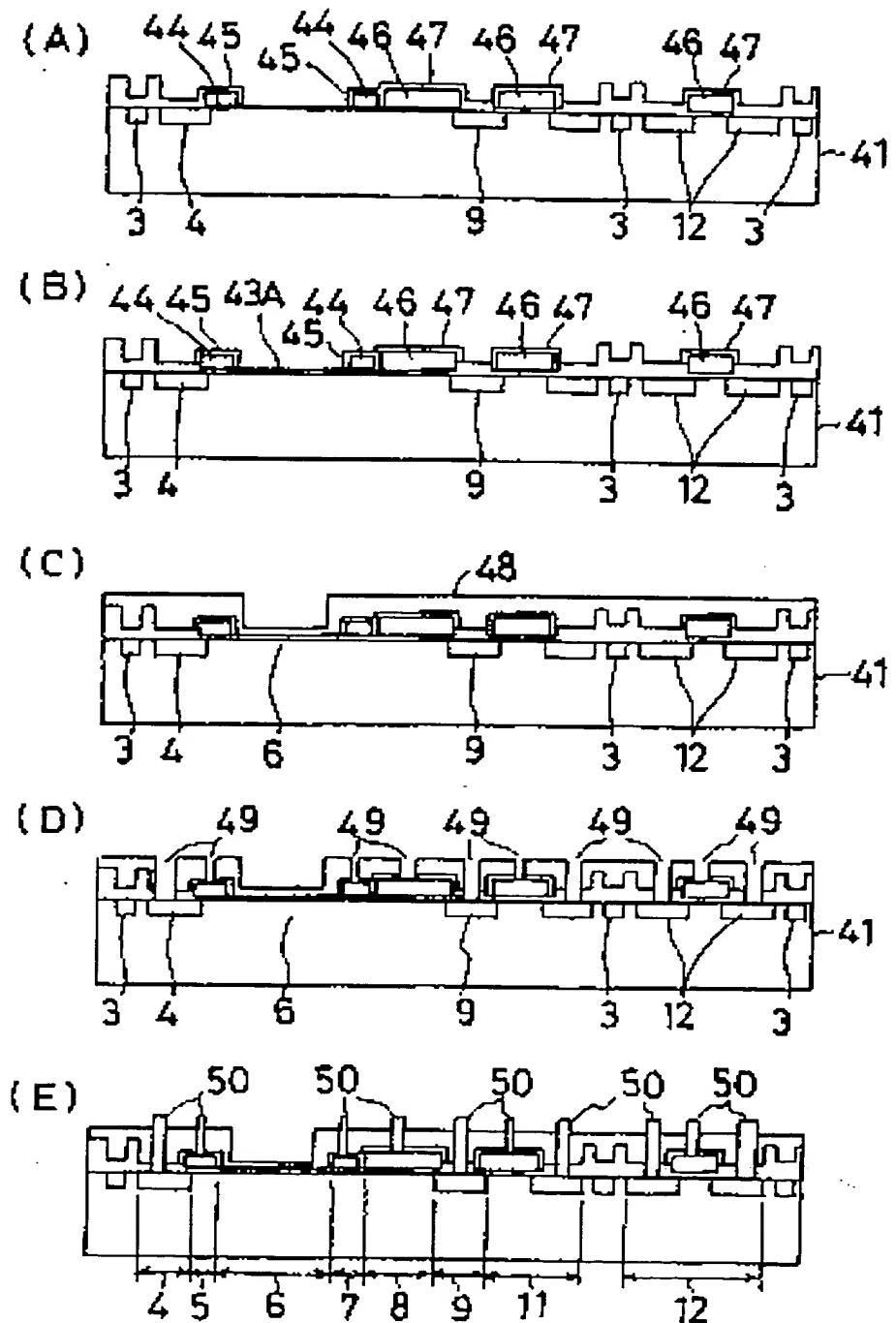


Fig. 17

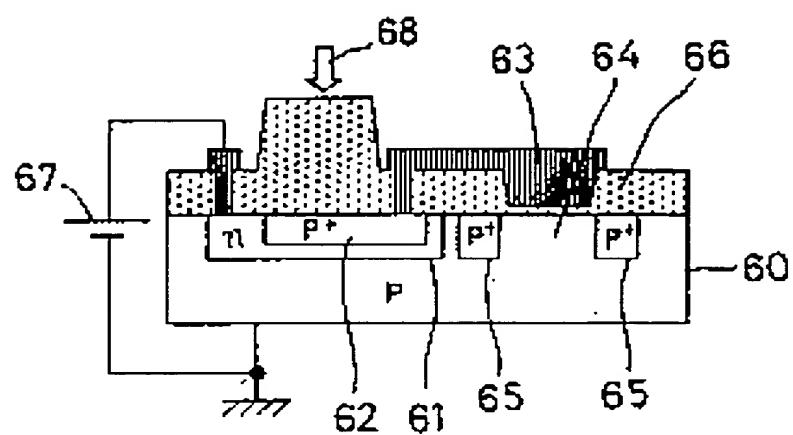


Fig. 18

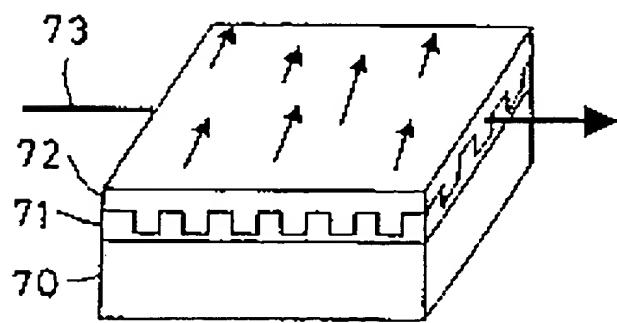


Fig. 19

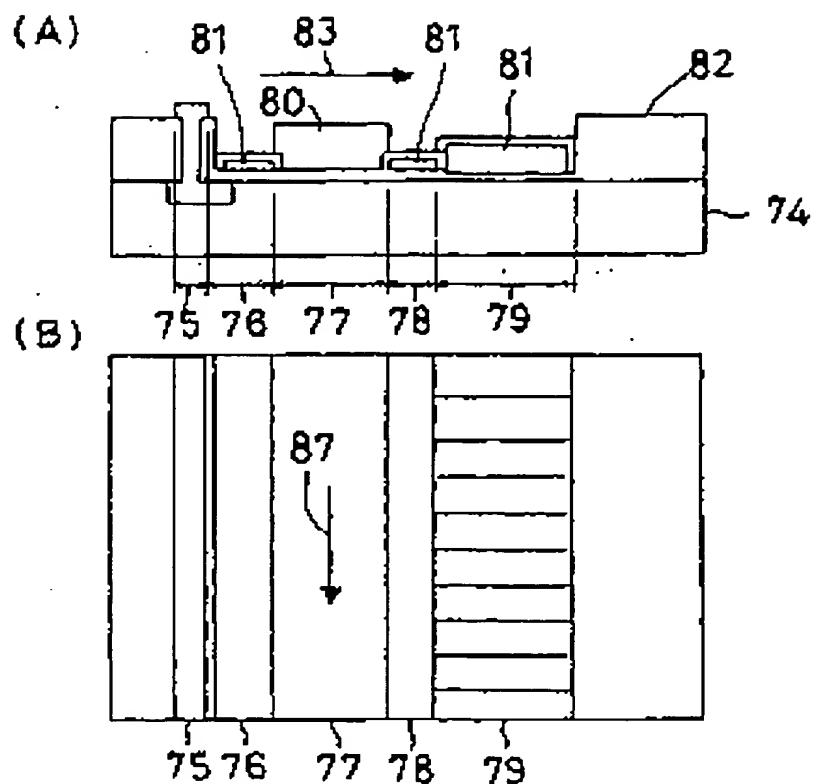


Fig. 20

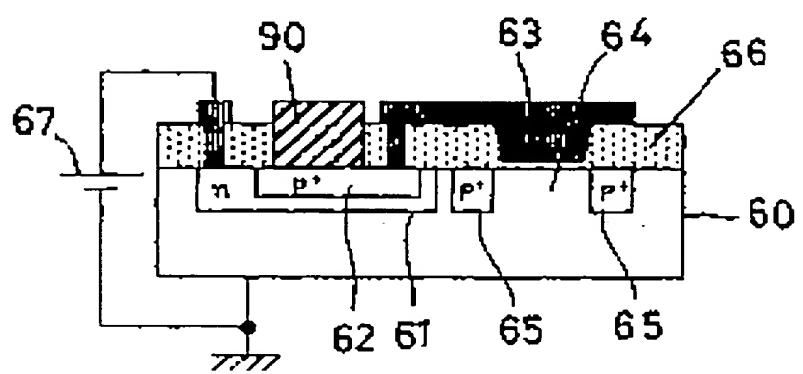


Fig.21

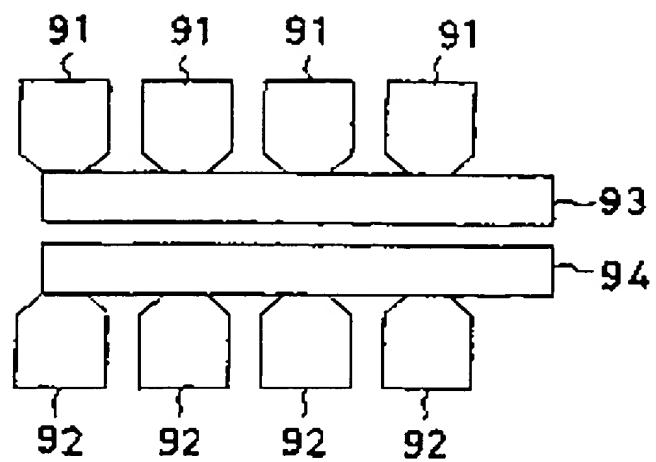
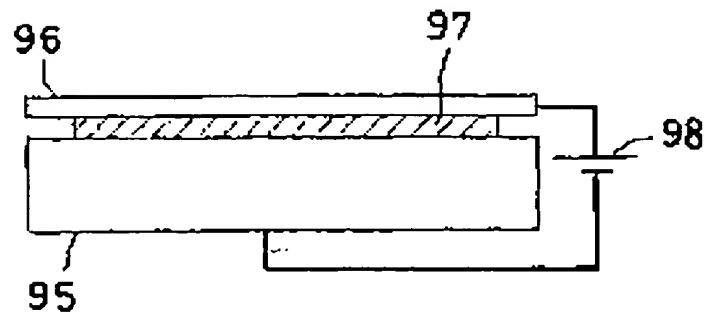
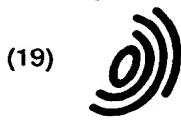


Fig.22







(19)

Eur pâisches Patentamt

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(11)

EP 0 881 486 A3

(12)

EUROPEAN PATENT APPLICATION

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02.12.1998 Bulletin 1998/49

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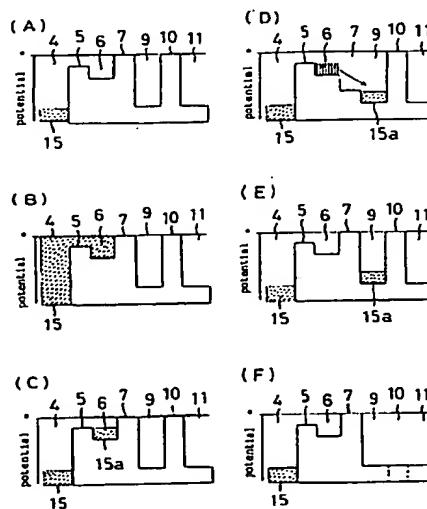
(74) Representative:
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81667 München (DE)

(54) Method for measuring physical phenomena or chemical phenomena and equipment thereof

(57) To provide a method and an equipment that can easily visualize various physical phenomena or chemical phenomena by simultaneously taking in, accumulating, and transferring the information at a plurality of points.

Electric charges are injected in potential wells constructed to vary the depth in accord with the magnitude of the physical or chemical quantity, and the physical or chemical quantity is converted into electric charges according to the depth of the potential wells.

Fig. 3



EP 0 881 486 A3



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	ANONYMOUS: "Charge Coupled Device Magnetic Field Sensor. April 1972." IBM TECHNICAL DISCLOSURE BULLETIN, vol. 14, no. 11, page 3420 XP002111424 New York, US * abstract *	1-4	G01N27/414 G01N27/00		
X	US 5 194 750 A (POPOVIC RADIVOJE) 16 March 1993 * column 2, line 56 - column 3, line 68; figures 1,3,11 * * column 6, line 63 - column 10, line 11; figures 1,3,11 *	1-4			
A	US 5 582 701 A (GEIS MICHAEL W ET AL) 10 December 1996 * column 6, line 63 - column 10, line 11; figure 5 *	1			
A	EP 0 771 104 A (NIPPON ELECTRIC CO) 2 May 1997 * column 6, line 63 - column 10, line 11; figures 4,7,10 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
A	EP 0 733 911 A (ANALOG DEVICES INC) 25 September 1996 * column 2, line 50 - column 3, line 38; figure 3 *	1	G01N		
		-/-			
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
MUNICH	5 August 1999	Mueller, T			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone	T : theory or principle underlying the invention				
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Office

EUROPEAN SEARCH REPORT

Application Number

EP 98 10 9769

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	<p>I.</p> <p>LUNDSTRÖM, E. HEDBORG, A. SPETZ, H. SUNDGREN, F. W. INQUIST: "ELECTRONIC NOSES BASED ON FIELD EFFECT STRUCTURES" SENSORS AND SENSORY SYSTEMS FOR AN ELECTRONIC NOSE, vol. 212, 1992, pages 303-319, XP002111425 DORDRECHT * column 2, line 50 - column 3, line 38; figure 1 *</p> <p>-----</p>	1
TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
MUNICH	5 August 1999	Mueller, T
CATEGORY OF CITED DOCUMENTS <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>		

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 98 10 9769

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05-08-1999

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5194750	A	16-03-1993		EP 0509141 A JP 5180918 A	21-10-1992 23-07-1993
US 5582701	A	10-12-1996		US 5374834 A US 5479035 A	20-12-1994 26-12-1995
EP 0771104	A	02-05-1997		JP 2877047 B JP 9121045 A US 5920346 A	31-03-1999 06-05-1997 06-07-1999
EP 0733911	A	25-09-1996		US 5591996 A JP 8293596 A	07-01-1997 05-11-1996